ION BEAM ACTIVATION FOR MATERIALS ANALYSIS: METHODS AND APPLICATIONS

T.W. Conlon
AERE Harwell Laboratory, Oxon. England.

Summary

A number of ion beam methods for materials analysis have been developed using Harwell's high voltage accelerators and these are currently being exploited for applications 'in house' and in industry. Ion beam activation is a relatively new area which has exhibited exceptional growth over the last few years. Activation by ion beams to produce a single dominant radioisotope as a surface label (thin layer activation or TLA) is becoming a mature technology offering ever increasing sensitivity for surface loss measurement (currently better than $0.1 \mu\text{m}$ or 10^{-7} cm^3 depending on the method of measurement) and remote monitoring of inaccessible components during studies of wear/erosion/corrosion/sputtering and the like. With the increasingly established credibility of the method has come the realisation that:

- (i) more complex and even multiple activation profiles can be used to extract more information on the characteristics of the surface loss process,
- (ii) that an analogous method can be used even on radiation sensitive materials through the newly established indirect recoil implantation process.
- (iii) that there is scope for treatment of truly immovable objects through the implantation of fission fragments,
- (iv) there is vast potential in the area of activation analysis.

The current state of development of these methods which greatly extend the scope of conventional TLA will be briefly reviewed. Current applications of these and TLA in industry are discussed.

Introduction

Thin layer activation is now widely used in Europe^{1,2} and in the USSR³ both as a research tool and as a service to industry. There is also growing interest in the USA⁴.

In the basic process (Figure 1) the service component or test material is activated with an ion beam, e.g. of protons, to produce a minute quantity of radioactive atoms, typically a few microcuries representing only 1 in 10^{10} of the substrate atoms, in a thin surface layer. This level of activity is found commonly for example in luminous watches and concrete walls, and requires only the most elementary handling precautions. The depth is precisely controlled by the ion beam energy and species, from less than $1 \mu\text{m}$ to several millimetres. A layer of $25 \mu\text{m}$ to $300 \mu\text{m}$ in the near surface or precisely positioned at a pre-determined depth below the surface is commonly used. Figure 2 shows a typical application, in which a cylinder liner has been activated around a narrow band, at a pre-determined position along the piston stroke. As material is worn away the gamma-ray activity from the layer, as measured sensitivity and directly through the wall and engine casing, decreases (case 1). Where a fluid circuit is available to transport wear debris to a central collection point, measurements can also be made there (case 2). The sensitivity achieved for case 1 is better than 1% of the layer thickness, e.g. less than $0.25 \mu\text{m}$ for a $25 \mu\text{m}$ layer. In case 2 it is much better, often less than 10^{-7} cc of substrate material (a few atomic layers) and substantially independent of the layer thickness. The method has overwhelming advantages compared with an older method based on bulk neutron activation. For example, a specific area (usually but not necessarily small) and specific depth of the wear surface is activated, which results in only trace quantities of activity being used; it allows direct measurement with high sensitivity which is not

Fig. 1. Thin layer activation of iron or steel by a proton beam.

possible with neutron activation; it can be applied to a much wider range of materials; and the most useful radioisotope for the end application can be chosen from a number which can be generated using different ion beams, with long or short half-lives as required.

Many of the components so far processed by TLA have been made of iron or steel, but active layers can be produced in a wide variety of materials including most of the common engineering materials. The following elements, their alloys and compounds are currently being studied: C, N, O, Al, Si, Ti, U, Cr, Fe, Co, Ni, Cu, W, Pb. Recoil activation (below) is applicable to any material.

Note that no modification to the surface or bulk properties of the material is likely due to the low particle flux usually involved, i.e. typically 10^{16} ions/cm². However it is essential that surface debris be removed from the activated region for successful measurement.

Fig. 2. Loss of activity is measured directly (1) or indirectly via a fluid circuit (2). No dismantling is required.

Technical Detail

When an ion beam enters a material the constituent charged particles rapidly lose energy, mainly by collisions with atomic electrons, and come to rest at the penetration depth as shown in Fig. 3a. The vast

majority of the particles follow this path. A very small number of particles follow the path shown in Fig. 3b, they interact with the nuclei of the material, induce a reaction and produce a radioactive species. The probability for a reaction is small compared to that for energy loss (about 1 in 10^6) and the two probabilities vary in different ways as a function of the energy as shown.

Suitable radionuclides can be produced from practically all elements and from a wide range of composite materials. The production of ^{56}Co in iron via the (p,n) reaction is commonly used, and this is illustrated by way of example in Fig. 3b. The half-life of ^{56}Co is 79 days; however, the monitoring period can extend over several half-lives so that the useful life of a component activated to ^{56}Co is about one year. (By use of different ion beams several different radioactive nuclei can be induced in iron, steels and other materials which extend the period over which measurements can be done to several and sometimes tens of years.) In the process of radioactive decay back to ^{56}Fe , ^{56}Co produces gamma-rays which range in energy between 0.551 MeV and 3.5 MeV. The higher γ -ray energies enable the surface loss of objects to be investigated in situ through up to 10 cm of iron, well beyond the range of X-ray penetration. While Fig. 3b illustrates the production of a 300 μm active layer, much thinner layers may be produced by 'angling' the beam into the target or by use of heavy ion reactions. Fig. 3c shows the profile of ^{58}Co induced in iron or steel by the $^{56}\text{Fe}(^7\text{Li},\alpha\text{n})$ reaction. More extensive layers may be produced depending on the range of material loss to be studied. Fig. 3d shows a sub-surface layer of ^{56}Co produced by $^{56}\text{Fe}(\text{p},\text{n})$ at 30 MeV. Such layers can be used to signal critical surface removal and in activation analysis (see below) to probe sub-surface concentrations of trace elements.

aid in developing condition monitoring capability and as a diagnostic tool for first wall problems in Tokamak systems¹. However it is in the non-nuclear industries that major use of the technique has grown recently¹. Fig. 4 illustrates the activation of a range of components for a wide spectrum of industrial users. In each case the ion beam is transported to the end of a beam line under vacuum, and transmitted through a thin metallic 'window' onto the component of interest. The diagram, which is schematic and not strictly to scale, illustrates, from the top: a spot irradiation on each of several cylinders in an engine block; an extended band of activity inside a rotating cylinder liner; a finely collimated spot at the end of a narrow tube; activation of a segment of a large piston ring; activation of a spot on the bend of a tube; large area activation of a plate by a swept beam.

For wear studies components which have been activated include cam followers, cylinder liners, valve seats, fuel injection equipment, steel tubes and bushes and a variety of machine tools. A major use of the technique is in engine testing of lubricants and fuels. It is possible in principle to study more than one component in the wear process by inducing different activities in each of several interacting components, e.g. cylinder liner, piston ring and in more fundamental studies the pin and disc of pin-on-disc machines. In this way it is also feasible to study the effects of adhesion and material transfer between components. One can foresee obvious applications of the process as a surface or sub-surface marker as an aid in the identification or relocation of objects. The measurement of the rate of movement or revolution of rollers or other moving parts is also possible since the activation can be made highly localised, although in general any desired area can be covered. Future developments in beam transport may allow spots only a few micrometres

Fig. 3 a. Energy loss versus depth for 13 MeV protons in iron.
 b. Profile of ^{56}Co activity produced by 13 MeV protons.
 c. Profile of ^{58}Co activity from 24 MeV ^7Li on iron compared to b.: ultra-thin layer.
 d. Profile of ^{56}Co activity from 30 MeV protons in iron compared to b.: 'buried' layer.

Applications

The current applications of TLA within the UK cover three major areas: wear, corrosion and erosion including electrical (plasma) erosion. The method has been used for a number of years as an R & D tool in the nuclear and electricity supply industries to study erosion and corrosion in fission reactor systems, as an

square to be activated.

In measuring corrosion rates the technique has been successfully used to measure uniform corrosion in acid corrodents as well as flow-assisted corrosion in fluid systems. Where pitting corrosion is a problem a more advanced version of TLA, described below, is indicated.

Fig. 4. Schematic showing the mounting and activation of several different components.

TLA is being applied to the measurement of the rate of erosion due to electrical plasma. In one experiment the titanium plate of the diverter chamber of DITE, an experimental Tokamak device, was activated and subsequently exposed to pulses of hydrogen ions at an equivalent temperature of 10^7 °C. The total activity remaining on the plate after each plasma pulse was measured and the technique proved sensitive enough to detect an erosion of 0.2 μ m after about 60 plasma pulses, corresponding to approximately one day's operation. The extension of the technique to the study of arcing erosion in Tokamaks and electrical switchgear is now under consideration.

Developments

The growing experience of the use of conventional TLA in the study and quantification of surface loss mechanisms whether due to mechanical, chemical or electrical phenomena has influenced strongly the direction of new developments of the process. The following more advanced analogues of TLA are under active development at Harwell.

(i) Multiple activation profiles^{1,5}

There are some mechanisms for surface removal for which material loss is substantially non-uniform; for example, certain well-recognised conditions of corrosion progress by local attack, with the formation of deep pits in which rapid chemical activity occurs in preference to the rest of the surface. The depth of such pits can dramatically exceed the average corrosion depth

determined for example by weight loss measurements or single layer activation and the detection of such local attack may be crucially important. A method of detecting the occurrence of such local attack has been used recently for the first time at Harwell. The method is based on the introduction to the surface of two (or more) layers of radioactivity with different depth profiles and different gamma-ray signatures. The two different active layers can be produced by activating the substrate separately with two different ion beams. However, by means of a deuteron beam at a suitable energy, two suitable layers can be produced in a single beam exposure as shown in Fig. 5a,b. The active species in this case are ^{56}Co produced by the $^{56}\text{Fe}(d,2n)$ reaction in a relatively shallow layer near the surface, and ^{57}Co produced by the $^{56}\text{Fe}(d,n)$ reaction to a depth of about 200 microns. The beam energy was 10.5 MeV. The detection of non-uniform surface loss is achieved by comparing the loss of ^{56}Co from the shallow layer with the loss of ^{57}Co from the deep layer by monitoring the increase in activity of the corrosion medium). If uniform loss of surface occurs then the locus of points for ^{56}Co loss versus ^{57}Co is as shown in Fig. 5c. If local attack occurs then the loss of ^{56}Co from the shallow layer will be lower than that expected for uniform loss, so that the shallow layer loss will be smaller than that indicated by the full line for a given deep layer loss, and indeed the locus of points generated in that case depends upon the shape of the pits thus formed. For example, the dashed line shows typical results for conical shaped pits, while the dotted line shows the results for deep spherical or bottle-shaped pits formed by material removed by undercutting the surface. Thus, by monitoring the changes in activity of the two layers, it is possible to detect not only the occurrence of non-uniform surface loss but also obtain information on the surface morphology. It is clear that more extensive information on pit size distribution and progression could be obtained with the use of more than two layers.

(ii) Fission fragment implantation⁶

Direct beam activation is suitable for metals and metallic alloys where the low level of activity required can be produced by a beam fluence which has a

Fig. 5. Double layer activation for measurement of uniform and pitting corrosion.

negligible effect on the surface and bulk properties of these materials. The method is, however, only of limited use for semi-conductors and insulators which have much lower thresholds for onset of radiation damage. Two methods of surface labelling which overcome this limitation have recently been proposed and are under development at Harwell. The first process, fission fragment implantation⁶, utilises a portable long-lived fission fragment source of, for example, ²⁵²Cf to generate fission fragments with suitable half-lives and γ -ray signatures to serve as TLA indicators. The profile for implantation into plastics of radioactive ¹⁴⁰Ba and ¹⁰³Rh produced following β - γ decay from primary fragments from a ²⁵²Cf source has been investigated⁶. The average depth of implantation is limited to about 15 μ m owing to the energy distribution of fragments from the source. The width of the distribution is controlled by the angular acceptance of the substrate. At present the shallow activation depths achieved and very long implantation times required (of the order of several weeks) are likely to restrict the industrial applications of this process.

(iii) Non-elastic recoil implantation^{7,8}

The process is closely related to a new method⁹ for the analysis and depth profiling of the light elements. The basic physics underlying both is similar and is present briefly below.

Consider a reaction $A(a,B)b$ where a is a heavy ion and B a heavy radioactive product recoiling from a sacrificial target into a substrate. The masses, Q -value and E_{cm} are chosen such that the maximum angle for emission of B , $\theta_c < 1$. θ_c is given by

$$\sin \theta = \left[\frac{Ab}{ab} \left(1 + \frac{\theta}{E_{cm}} \right) \right]^{\frac{1}{2}} \quad (1)$$

The energy of the recoil species is single valued only at θ_c and given by

$$E_c = \frac{aB}{(a+A)^2} (1 - \sin^2 \theta_c) E_{in} \quad (2)$$

It can be shown⁹ that the yield of B is a maximum at θ_c and zero at 0° for both isotropic and $1/\sin \theta$ type c.m. angular distribution and that the multiple scattering of the beam is negligible beyond θ_b , where $\theta_b \ll \theta_c$. Thus by choosing suitable reactions e.g. $H(^7Li, ^7Be)n$ a wide range of radioactive products can be implanted with high efficiency while avoiding direct beam effects on the substrate. The depth distribution can be controlled by varying the angular acceptance of the substrate.

(iv) Ion beam activation analysis and depth profiling of light elements

Light ion beams ($M \leq 4$) do not in general produce useful radioactive products from light elements ($M < 19$) present in trace quantities in a substrate. Bulk activation analysis of such elements has been demonstrated¹⁰ by the use of 'heavy' ($M > 4$ and typically 7 - 20) ions. However such reactions were considered unsuitable for depth profiling owing to the recoil kinematic effects which destroy the correlation between initial profile and final activated product distribution. This is generally true but the situation can be saved⁹ by choosing reactions such that the desired recoil product is kinematically confined to a maximum or critical angle and by observing events close to that angle. Thus near θ_c

(a) The recoil energy is single valued (eqn. 2 above) giving a one-to-one relationship between energy and depth through the application of the stopping power equation.

(b) The yield is also high.

The method, called non-elastic recoil analysis, is generically similar to elastic recoil analysis and can be used to depth profile a number of light elements simultaneously and with high efficiency.

Fig. 6. Recoil activation (implantation) - an alternative to direct activation for certain active species and substrates

Activation by ion beam for bulk analysis is often complicated by surface contaminants. Sub-surface activation analogous to the use of buried layers discussed above (Fig. 3d), may overcome this problem. The natural width of the excitation function acts like a resonance to selectively activate a range of depths at a point in the sample determined by the incident energy. Heavy and light ions may be used.

Both of these concepts are under active development.

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