THE APPLICATION OF A CYCLOTRON IN MATERIALS RESEARCH AT THE IAM OF THE EUROPEAN COMMISSION

M.F. STROOSNIJDER

Institute for Advanced Materials, Joint Research Centre of the European Commission, 21020 Ispra (VA), Italy

The cyclotron of the Institute for Advanced Materials-Ispra site of the European Commission was initially used for materials questions related to nuclear fusion technology. However, this activity has declined and the use of the cyclotron has been extended to other fields. These include the use of Thin Layer Activation (TLA) for wear and corrosion studies. A special application is the use of TLA for high temperature cyclic oxidation testing. After a general introduction on spallation by thermal cycling, the use of TLA to measure spallation of protective surface layers by thermal cycling is discussed. Its use is illustrated with the study of the spallation behaviour of powder metallurgically produced chromium. Due to its intrinsic properties, TLA can contribute to a greater scientific understanding of material degradation by thermal cycling and it can provide a more reliable assessment of the service lives of technical components.

1. Introduction

The cyclotron of the Institute for Advanced Materials-Ispra site of the European Commission is a Scanditronix variable energy MC-40 cyclotron. The cyclotron can accelerate protons and α-particles in the energy range of 10 to 39 MeV and deuterons from 5 to 19 MeV. The cyclotron facilities include also three irradiation halls. At present six beamlines are fully equiped. Initially, the cyclotron was essentially used for materials questions related to nuclear fusion technology. At present this activity is mainly based on martensitic steels, but also new advanced materials, including ceramic-ceramic composites, e.g. SiC/SiC. In recent years, the nuclear fusion activity has declined and the use of the cyclotron has been extended to isotope production for medical applications, especially the commercial production of ^{123}I. Another major activity is the production and use of tracers for environmental studies in collaboration with the Environment Institute of the European Commission. This includes toxicological studies of Pt, Pd and Rh related to automobile catalytic converters [1]. The main activity nowadays is material studies, in particular the use of Thin Layer Activation (TLA) for various wear and corrosion studies.

The principal basis of TLA is the creation of radionuclides in a surface layer to a well defined depth of a selected area, by exposure to a high energy charged particle beam [2,3]. If the material is subjected to mechanical or chemical degradation such as wear or corrosion, any loss of the activated material will result in a loss in radio-activity of the activated component. This reduction in signal can be directly related to mass loss or thickness reduction; the removed material debris, collected in a filter or fluid sample, also gives a measure of material degradation. The latter approach, in general, results in a higher sensitivity [3]. The specific properties of TLA [3] include area selectivity, high sensitivity, speed and applicability as a non-contact in-situ method. Due to its specific properties, TLA can contribute significantly to monitor surface degradation in both research and industrial applications. The technique itself has been used for some time, especially related to applications for the automotive and engine industry including engine testing of lubricants and fuels [e.g. 4,5]. Besides using TLA for wear testing both for industrial purposes as well as for the development of wear resistant materials, the Institute for Advanced Materials is also active in improving its application and extending it to new fields. In this area the Institute for Advanced materials benefits strongly from its combination of materials oriented research and the possession of a cyclotron. One of the special applications is that for high temperature cyclic corrosion testing.

In the present paper, a brief overview of high temperature cyclic corrosion and the use of TLA in cyclic corrosion testing is given. This is illustrated with an example of the cyclic corrosion behaviour of chromium using TLA.

2. Cyclic corrosion

The potential of alloys and coatings to resist high temperature corrosion generally depends on their potential to form and maintain a protective oxide scale, e.g. Cr_2O_3 or Al_2O_3 [6,7]. However, service mechanical stresses, as generally encountered under operating conditions, may undermine the scale stability causing cracking and spallation, leading to accelerated corrosive attack of the underlying material. The spalled fragments cause problems in that they may lead to erosion or blocking of gas flows and/or contamination of products. One of the commonest sources of mechanical stress is due to thermal cycling as a consequence of the difference in thermal expansion coefficients of the oxide scale and material. Spallation of protective surface layers due to thermal cycling is a significant problem in a wide range of technological applications, ranging from coatings on gas turbine blades, heat exchanger applications to oxide fuel cells.

The resistance of materials to thermal cycling is determined from cyclic corrosion tests, in which a sample is exposed at a test temperature, which is changed with time in a periodic way, often simulating the industrial conditions. The cyclic corrosion literature primarily deals with the qualitative ranking of materials, determined mostly by mass change. It should be mentioned that the relation between mass change and material loss, the actual parameter one wants to measure, can be very complicated. This is caused by the fact that mass change results from various processes, e.g. oxygen uptake due to normal corrosion, loss of oxide (i.e. oxygen and metal) caused by localized spallation and oxygen uptake due to healing of the spalled regions possibly with different kinetics than the normal corrosion. Other complications arise when samples are not uniform, for example they have a coating on only one side or there are geometrical irregularities, such as sample edges. In such circumstances the amount of spalled material can be roughly estimated by optical determination, or by cross-sectional determination. However, such methods can be highly inaccurate and/or laborious [8]. The understanding of material degradation due to cyclic corrosion is limited and not yet sufficient to allow the processes to be modelled in a reliable fashion. The main difficulty arises from the fact that the variable to be measured, material consumption, can be determined only with great difficulty and low accuracy [9]. A way of measuring spalled material loss directly is by using TLA.

The principle of the TLA application for cyclic corrosion testing as developed in the Institute for Advanced Materials [10,11] is to subject an activated material sample to repeated heating and cooling cycles in a corrosive environment. The approach is used in which the activity of the spalled material, instead of the sample, is measured. In this way the sensitivity of the method is significantly higher and can be in the range of ng/cm^2 [11]. The detached material is accumulated in a spall collector. After a certain pre-determined number of heating and cooling cycles, the spall collector containing the spalled material is removed to determine its radiation intensity as a function of the γ-energy. The γ-intensity, corrected for the natural decay, is a direct indication of the spalled material loss. After these measurements, the cyclic test is continued. Fig. 1 shows some of the specialized test facilities which are used for high temperature cyclic corrosion studies using TLA.

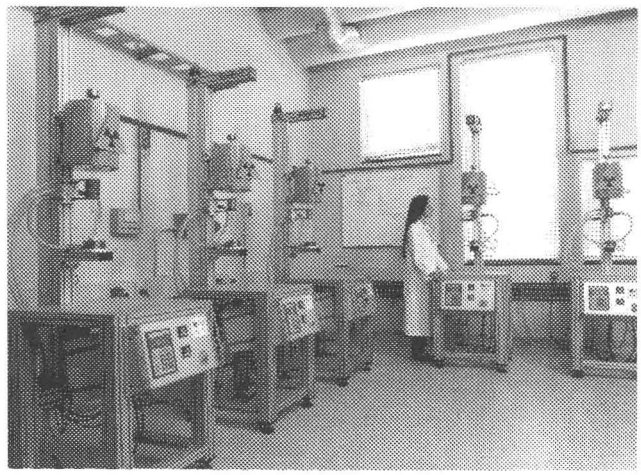

Fig. 1: Test facilities for high temperature cyclic corrosion testing using TLA.

3. Example of TLA for cyclic corrosion testing

As an example, the use of TLA to study the spallation behaviour of powder metallurgically produced chromium will be presented. The investigated material was commercial Ducropur chromium, a rather new material produced by powder metallurgical route, by which semi-finished or finished products with chromium as the main alloy constituent are achievable [12].

For wear applications, radionuclides of elements which are no material constituent elements can be employed (e.g. ^{56}Co produced by a (p,n) reaction of ^{56}Fe). However, for corrosion studies radionuclides must be chosen which participate in the formation of the oxide scale. Additionally, the half-life of the isotope should be long enough to follow the phenomena for a technically relevant time, i.e. 1000 h or more. This limits the choice to the isotope ^{51}Cr which has a half-life of 27.7 days and emits specific γ-radiation of 320 KeV. The optimum activation conditions were determined in a rather extensive study [13,14]. On this basis, activation of the samples was performed using 10 MeV deuterons at normal incidence in the centre of one principal coupon face. A surface layer was activated homogeneously to a depth of about 120 µm. Fig. 2 shows a typical γ-spectrum from an activated sample. Besides ^{51}Cr, only ^{48}V, ^{52}Mn and ^{54}Mn, arising from other nuclear reactions, are present. ^{51}Cr is produced via 3 different reactions as a result of the activation of natural Cr by deuterons: ^{50}Cr(d,p)^{51}Cr; ^{52}Cr(d,p2n)^{51}Cr and ^{50}Cr(d,n)^{51}Mn(β$^+$)^{51}Cr [13].

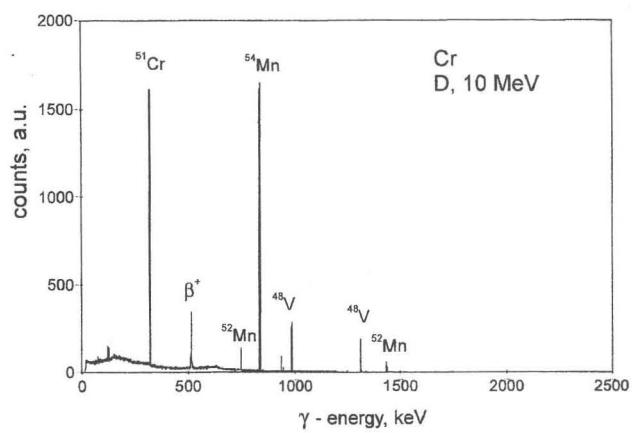

Fig. 2: γ-spectrum obtained from the chromium substrate by activation with 10 MeV deuterons.

The facilities for cyclic corrosion testing using TLA have been described in detail elsewhere [11]. Thermal cycling was performed in air and each thermal cycle consisted of heating to the test temperature and maintaining this for 1 h followed by cooling to about 30 °C with a total cooling time of 12 min. Test temperatures were chosen between 800 °C and 1000 °C. The detached material was accumulated in a spall collector which was removed after various numbers of cycles to determine its radioactivity of ^{51}Cr in a lead shielded measuring system integrating a germanium detector. The efficiency of the γ-spectrometer system was calibrated regularly, using a standard emitting source of ^{137}Cs. The γ-intensity of the spalled material was corrected for natural decay, expressed as the ratio of the ^{51}Cr-activity of the original sample ("relative activity") and recalculated to give the material loss.

The influence of the maximum test temperature in the thermal cycle is presented in Fig. 3 for 800 °C, 900 °C and 1000 °C. The spalled material was determined by XRD to be Cr_2O_3. The spallation at 1000 °C appeared to follow linear kinetics with a Cr spallation rate of approximately 20 μg/(cm^2 cycle). The spallation behaviour at 900 °C was more irregular. However, long term testing [15] showed that also in this case an approximately linear behaviour applies with a Cr spallation rate of about 0.4 μg/(cm^2 cycle). In the case of a maximum test temperature of 800 °C, no spallation could be observed.

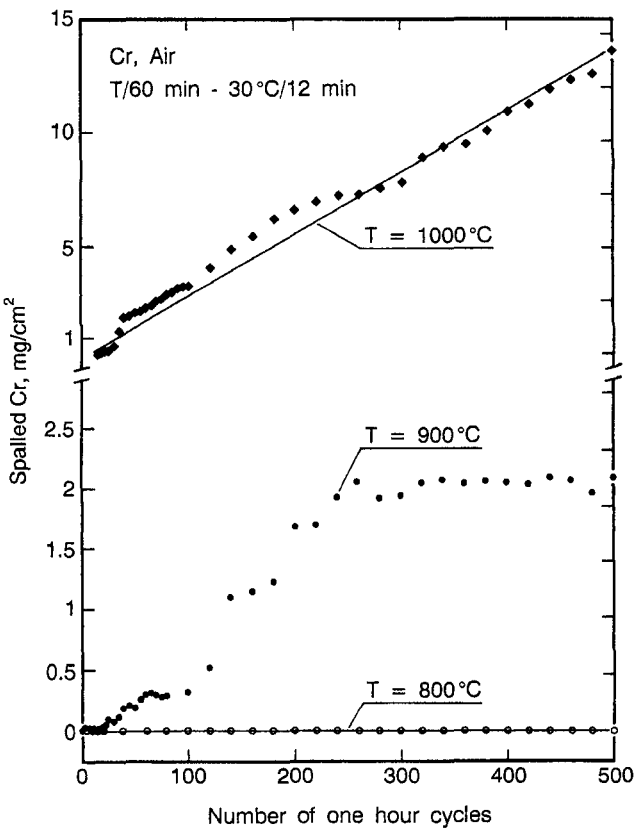

Fig. 3: Spallation behaviour of chromium due to thermal cycling from various maximum temperatures to ambient temperature.

It should be noted that these spallation rates are related to the activated area in the centre of the sample. In agreement with observations in literature, the spallation behaviour near the edges was observed to be different. Thus, the present data are for flat surfaces only, representative of plant walls, without the distorting influence of corners and edges on the rather tiny corrosion samples. This aspect especially and the direct relation of these data to material released from the surface, make the obtained data more relevant to many engineering needs than data obtained with other methods, such as gravimetry.

4. Summary and concluding remarks

The use of TLA has generally been restricted to the field of wear testing related to automotive applications. However, the technique shows an enormous potential for diversification and further development. The method has significant benefits when used to measure spallation of protective surface layers exposed to thermal cycling. These include high sensitivity and the area selectivity, which offers the possibility to study the spallation on flat surfaces, representative of plant walls, without the distorting influence of corners and edges on the rather tiny corrosion samples. Additionally, this gives the possibility for mechanistic studies on the role of geometric factors, such as specimen curvature and size, which might be a significant help in standardizing test methods. Another specific property of TLA is that the data have a direct relation to material lost from the surface, the actual parameter one often wants to measure from an engineering point of view.

The use of TLA as an experimental method for spallation studies has not been exploited fully and it offers considerable potential for further development. It can contribute both to mechanistic studies, as well as to the generation of engineering data. In this context it should also be mentioned that the technique has a wide scope of application and can be used in the laboratory, as well as on technical components in industrial applications. However, due to its need for specialized facilities and, to some extent, also to nuclear safety aspects, the application of TLA for cyclic corrosion testing is at present only performed on a day to day basis at the Institute for Advanced Materials of the European Commission.

Acknowledgements

The author is grateful to Dr. D.B. Meadowcroft, ERA Technology Ltd., for valuable discussions during the preparation of the manuscript. The assistance of the staff of IAM-Ispra, in particular Mrs. R. Bisconti and Messrs. A. Bervoets, P. Dominke, P. Laguzzi, G. Macchi, R. Müller, I. Murris, U. Pesce, G. Pisoni and R. Valle, is gratefully acknowledged.

References

1. R. Pietra, E. Sabbioni, G. Pozzi, M.F. Stroosnijder, M. Bonardi, L. Ulrici and J. Kucera, Submitted for publication in *J. Radioanal. Nucl. Chem.*
2. T.W. Conlon, *Contemp. Phys.* 26 (1985) 521.
3. M.F. Stroosnijder, in *"Application of Particle and Laser Beams in Materials Technology"*, P. Misaelides (ed.), Kluwer Press, 1995, p. 399.
4. T. Kosako and K. Nishimura, *Nucl. Instr. and Meth.* B56/57 (1991) 900.
5. P. Fehsenfeld, A. Kleinrahm and H. Schweickert, *J. Radioanal. Nucl. Chem. Art.* 160 (1992) 141.
6. P. Kofstad, *"High Temperature Corrosion"*, Elsevier, 1988.
7. M.F. Stroosnijder, R. Mevrel and M.J. Bennett, *Materials at High Temperatures* 12 (1994) 53.
8. M. Schütze, V. Guttmann and M.F. Stroosnijder, in *"Guidelines for Methods of Testing and Research in High Temperature Corrosion"*, H.J. Grabke and D.B. Meadowcroft (eds.), EFC publication no. 14, The Institute of Materials, 1995, p.104.
9. C.E. Lowell, C.A. Barrett, R.W. Palmer, J.V. Auping and H.B. Probst, *Oxid. Met.* 36 (1991) 81.
10. M.F. Stroosnijder and G. Macchi, International Patent pending.
11. M.F. Stroosnijder and G. Macchi, *Nucl. Instr. and Meth.* B100 (1995) 155.
12. H.P. Martinz, W. Köck and T. Sakaki, *J. de Physique* IV, 3 (1993) 205.
13. R. Bisconti, K. Casteleyn, M. Castiglioni, F. Fossati, L. Manes and M.F. Stroosnijder, *Nucl. Instr. and Meth.* B 88 (1994) p. 282.
14. G. Laguzzi, R. Bisconti, G. Macchi and M.F. Stroosnijder, *Nucl. Instr. and Meth.* B100 (1995) 540.
15. M.F. Stroosnijder, I. Murris and G. Macchi, to be published.