GAS FLOW PROPORTIONAL COUNTER FOR LOW TEMPERATURE CONVERSION ELECTRON MÖSSBAUER SPECTROSCOPY

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The construction of a simple gas flow proportional counter suitable for operation between 100 K and 400 K without the need for an evacuated cryogenic system is described. Different gas mixtures have been studied over the temperature range and it was found that He/5% CO is most suitable at 100 K. The system has been tested using standard foils to obtain the optimum operating conditions. Low concentration iron based samples have also been studied to show the importance of investigating surface phenomena at different temperatures.

1. Introduction

The use of conversion electron Mössbauer spectroscopy (CEMS), as a technique for studying the surface properties of materials, is steadily gaining popularity especially as an analytical technique applied to problems encountered in the industrial environment. In particular, the integral CEMS method, which incorporates the detection of all conversion electrons without energy discrimination, is now commonly used for the study of ion-implanted materials, supported iron clusters, thin films, heterogeneous catalysis, surface wear resistance and identification of corrosion products in iron based metals and alloys. The CEMS technique is particularly well suited to these fields of study since interaction depths are typically about 500 nm which corresponds to the probe depth of the detected conversion electrons. The large signal-to-noise ratio (S/N), obtained using the CEMS geometry, is also advantageous since in most materials investigated, the $^{57}\text{Fe}$ concentration is very small over the 500 nm near surface region. Even in materials containing the natural abundance of $^{57}\text{Fe}$, high quality spectra can still be obtained in less than one day. Such is the case for products formed during the natural corrosion processes in steels, for example. In iron-implanted materials, implanted fluences of less than $10^{16}^{57}\text{Fe}$ atoms cm$^{-2}$ over a 50 nm thickness result in very long experimental recording times if the normal transmission geometry is used.

Present investigations of iron-implanted polymers, corrosion processes in steels and iron-doped semiconductors have lead us to develop several CEMS systems. In each case the design and construction of the gas flow proportional counters have been undertaken in order to obtain maximum efficiency and count rate at room and low temperatures. This requirement was especially necessary for studies of iron-doped indium phosphide samples in which the concentration of $^{57}\text{Fe}$ is about $3 \times 10^{11}$ atoms cm$^{-2}$ over 100 nm thickness.

2. Design considerations

Much work has been previously reported on the development of electron detectors suitable for surface studies [1–9] and generally, the gas flow proportional counter has been used for detection of the low energy electrons. Its construction and operation at room temperature is simple and it can easily be built to suit the geometry of the particular sample being investigated. In general, the detector geometry, construction material, gas, shielding and anode potential are all well understood. Operating the detectors at low temperatures has presented problems, however, particularly with the quench gas whose vapor pressure is significantly lowered at 100 K. Low temperature operation generally requires the detector to be mounted in an evacuated cryostat and this can limit the number of experiments which can be undertaken at any one time.

It is often important to be able to perform CEMS experiments over a large temperature range and, in many cases, without moving the sample between different sets of equipment. For example, the room temperature study of the many forms of iron oxides, which are often found on the surfaces of materials, are difficult to separately identify. One typical case is the identification of the $\beta$ and $\gamma$ phases of FeOOH, which at room temperature have very similar quadrupole splitting and isomer shift. At liquid nitrogen temperatures, however, each phase can be easily identified since $\beta$-FeOOH is
magnetically ordered and $\gamma$-FeOOH is not. Super-paramagnetism is also often observed in surface studies and is due to small aggregates of the iron compounds present. In particular, this interaction is observed in high fluence ($10^{17} \text{ }^{57}\text{Fe cm}^{-2}$) iron-implanted samples. Room temperature experiments do not always allow the identification of the superparamagnetic compound. However, cooling the samples slows down the magnetic fluctuations enabling the hyperfine spectra to be better resolved.

This paper reports on the construction of a gas flow proportional counter which can be operated between 100 K and 400 K without the need for an evacuated cryogenic system. Furthermore, the detector can be operated within this temperature range without the need to move the sample or alter the detector geometry. The simple construction and operation of the detector allows several Mössbauer systems to be run simultaneously if more than one source, transducer, and associated electronics are available. For example, separate detectors can be attached to each end of one Mössbauer transducer if two sources are available. The only maintenance required for low temperature operation is to refill the liquid nitrogen dewars every twelve hours. Because no vacuum system is required, there are no pump vibrations present in the vicinity of the experiments.

3. Construction of the proportional counter

The detector has been constructed using the combined features reported by other investigators [1–4] and in some cases we have found minor modification to be helpful. The general design is similar to that described by Spijkerman [2]. Fig. 1 shows a sketch of the detector. The chassis consists of rectangular aluminium frame, (61 mm × 38 mm × 12 mm), with gas inlet and outlet pipes sealed on either side and a high voltage connector sealed on one end. The chassis is in good electrical contact with the outer shield of the high voltage connector which is used as the detector cathode maintained at ground potential. A solid lucite block, (25 mm × 25 mm × 12 mm) is made to fit inside the chassis and is used to support the anode and the sample. A 13 mm diameter cylindrical hole is cut through the lucite to form the sensitive detecting volume. Two 2 mm deep grooves, 4 mm apart, are cut lengthwise along the lucite in order to facilitate easy installation of the continuous 0.025 mm diameter tungsten anode. The anode is threaded through four thin, short pieces of teflon tubing which are placed in the grooves of the lucite block. This is done to insulate the anode from the cylindrical wall of the sensitive volume which has been painted with a thin coating of aluminium paint. The aluminium paint ensures that the lucite block is in good electrical contact with the aluminium chassis and prevents charge buildup inside the detector around the sensitive volume. The anode is pulled tight inside the lucite block and each end is soldered to the high voltage connector. Care is taken to ensure a clean, smooth soldered joint in order to avoid spurious discharges around the connector. Although tungsten does not solder easily, the very thin anode wire used in the detector is able to be secured by the solidified solder on the high voltage connector. The only exposed section of the anode, $= 7$ mm in length, is well inside the diameter of the sensitive volume.

The gamma ray entrance window (top), is covered with a 4 mm thick rectangular lucite plate in order to absorb the 6.4 keV K X-rays from the $^{57}\text{Co}$ source. This plate is thicker than normally used and was found to be necessary for use with the 100 mCi $^{57}\text{Co}$ in Rh source. A thin (0.0025") aluminium foil is placed next to the lucite plate to help increase the efficiency of the detector. A rectangular aluminium plate is then placed over the top
and secured to the chassis with 4 screws. A 13 mm hole in the aluminium plate is centered above the sensitive volume, and a rubber gasket, 1 mm thick, is sandwiched between the detector chassis and lucite plate in order to maintain an airtight seal.

The sample under investigation is loaded from the bottom onto the lucite block and is therefore 2 mm from the anode. The sample is sandwiched between two thin sheets of aluminium foil in order to properly ground it to the detector chassis. A 13 mm diameter hole in the foil closest to the anode allows passage of the electrons from the sample into the sensitive volume. Maintaining the sample at ground potential was found to be important for efficient and continuous detection over long periods of time.

If experiments are to be undertaken at room temperature only, the bottom of the detector is assembled using a rubber gasket, lucite and aluminium sheets and an aluminium plate screwed to the chassis. However, in most cases a slightly modified version is assembled in order to allow low temperature spectra to be recorded. In this case the 4 mm thick lucite plate and thin aluminium foil are removed. This side of the chassis is then covered with a thicker piece (0.001") of aluminium foil which is in contact with the back surface of the sample. A layer of thermal compound between the sample and the aluminium foil assures good thermal contact. A rubber gasket and a 3 mm thick aluminium plate are used to seal the detector. However, a 1" diameter hole is cut in the gasket and aluminium plate on the bottom of the detector centered on the sample. A cylindrical copper rod, 1" in diameter and 24" long, is then inserted into the hole and pushed against the aluminium foil covering the sample. Again thermal compound is used to make good thermal contact between the aluminium foil and the cold finger. A large polyvinyl chloride collar with a 1" diameter hole in it is secured to the copper rod just below the detector. Two aluminium brackets placed over the top of the detector are secured to the collar to prevent the detector from separating from the copper rod during the experiment. A silicon diode thermometer and a 34 Ω resistor are inserted into two holes drilled into the copper rod from the side. The thermometer is situated 4 mm below the sample and the resistor, used to heat the sample between 100 K and 400 K, is inserted 30 mm below the sample. The collar supporting the detector and copper rod is then securely attached to the outer frame of the Mössbauer transducer. This helps eliminate unwanted relative vibrations between the absorber and the source which is attached to the central drive rod of the transducer. A graded shield with a 13 mm diameter hole is placed between the detector and the source in order to collimate the gamma rays to the surface of the sample under investigation. This helps reduce the number of photoelectrons emitted from the detector material. For experiments at temperatures below 300 K, the long copper rod is immersed in a 25 liter dewar of liquid nitrogen. Fig. 2 shows the arrangement of the equipment for low temperature operation.

4. Detector operation

In order to test the operation of the detector particularly at 100 K, several different gas mixtures were studied. A low pressure gas flow regulator (Matheson Model 3702, 0-5 psig) was used to control the flow rate to ±0.1 cm³ min⁻¹. Flow rates between zero and 20 cm³ min⁻¹ were measured with a mass flow transducer (Hastings Model LF20) inserted into the gas line to the detector. Very stable gas flow rates were found to be important in order to maintain constant detector gain. Before each experiment both the gas flow rate and high voltage were adjusted to give a suitable detector gain. The main amplifier gain was then adjusted in an attempt to sufficiently separate the low energy noise from the resonantly emitted conversion electrons. Two standard absorbers, 30% ⁵⁷Fe in Rh foil and 95% enriched iron foil were used to test and calibrate the equipment. For the latter foil a typical S/N was about 20 to 1 and the linewidth observed was 0.265 mm s⁻¹ [10]. A 100
mCi $^{57}$Co in rhodium source was used and was placed about 20 mm from the absorber and driven in sinusoidal mode by the transducer.

Gas mixtures of He/1% CH$_4$, He/5% CH$_4$, He/10% CH$_4$, He/5% CO as well as pure helium were studied at temperatures between 100 K and 300 K and at 400 K in an attempt to evaluate the best operating characteristics for detecting electrons. A gas mixture of Ar/5% CH$_4$ was also used to determine the detector's sensitivity to X-rays at different temperatures. In general, it was found that all gases investigated were suitable for operation at temperatures of 300 K and 400 K. The pulse height spectra of the radiation emitted from the surface of a 30% enriched Fe in Rh foil were studied on and off resonance for each gas mixture. At temperatures of 100 K, 300 K and 400 K flow rates and applied anode potential were varied to give the best resolution between the resonant electron peak and the lower energy background. At room temperature and a flow rate of 4 cm$^3$ min$^{-1}$ typical anode voltages ranged from 600 V for pure helium to 1100 V for He/10% CH$_4$. For He/5% CO flowing at 4 cm$^3$ min$^{-1}$ an anode voltage of 900 V gave similar pulse height spectra to the CH$_4$ quench gas mixtures. The range of voltage for suitable operation at constant gas flow was much smaller ($\approx 30$ V) for pure helium than for He/10% CH$_4$ and He/5% CO ($\equiv 150$ V). Each of the helium based gas mixtures gave fairly well resolved electron peaks at 300 K and 400 K. At 100 K the resonant electron peak was not resolvable from the background for the gas mixtures of He/1% CH$_4$ and He/5% CH$_4$ even at gas flows of 8 cm$^3$ min$^{-1}$ and anode voltage just below the breakdown threshold. Mössbauer spectra could be recorded with the enriched foil even though the lower energy discriminator was difficult to set accurately. However in each case the signal-to-noise ratio was very small.

From the study using pure helium gas, no suitable gas flow and anode voltage setting were found. Multiple discharges inside the detector were evident. The gas mixture of He/10% CH$_4$ gave marginally better pulse height spectra than the other methane quench gases with the resonant electron peak just observable on the noise. The He/5% CO mixture did allow the electron peak to be better resolved and the lower level discriminator could be accurately set. The best results were found with a gas flow of 8 cm$^3$ min$^{-1}$ and an anode potential of 1250 V. For all low temperature studies, the gain of the main amplifier had to be increased by a factor of 20 to 1 K. Higher amplifier gains resulted in a large amount of noise which dramatically decreased the quality of the pulse height spectrum.

The gas mixture of Ar/5% CH$_4$ was investigated over the temperature range also. In each case the X-ray Mössbauer spectra have been recorded using samples of corroded weathering steel and these results will be published at a later time.

Room temperature spectra are normally recorded using pure helium gas flowing at 4 cm$^3$ min$^{-1}$ and an anode potential of 600 V. At low temperatures (less than 150 K), He/5% CO was used flowing at about 8 cm$^3$ min$^{-1}$. The anode voltage was about 1250 V. Once the copper rod was inserted into the liquid nitrogen, a sample temperature of about 85 K was reached within 20 min. The temperature controller was then used to maintain a stable temperature to $\pm 0.2$ K. Although the minimum temperature reached at the absorber was 85 K, it was found to be more convenient to use the temperature controller to maintain a stabilized temperature of 100 K. This compensates for the increase in temperature due to the decreasing liquid nitrogen level in the dewar and also allowed experiments to run for periods of about 12 h without having to add more nitrogen. No cracking of the lucite block was observed during cold operation. The detector chassd itself was not insulated in any way and a small amount of ice collected on the outside surface. This was scraped off daily, especially around the region of the gamma ray entrance window. No moisture was found inside the detector on completion of the experiments. This indicates that the rubber gaskets formed a good air-tight seal at low temperatures. At 100 K, experimental runs up to seven days have been regularly performed. Over this period, no adjustment of the high voltage was necessary as has been reported previously [8], and this is thought to be due principally to having the detector well sealed to prevent moisture from entering the region around the sample and anode. After two days operation, a small quantity of ice was often seen to form inside the gas inlet line at the detector chassis. This is due to moisture contained in the gas mixtures ($\approx 40$ ppm water vapor). If left, a partial blockage of the gas inlet resulted in a decrease in gas flow rate and a subsequent decrease in detector gain. The ice was generally removed every two days by quickly disconnecting the gas inlet line and scraping out the tube. Normal detector operation subsequently was observed. This problem may have been the reason why previous investigators have reported the need to increase the high voltage at the anode every one or two days in order to maintain consistent operation of their detectors at low temperatures. Increasing the anode potential compensates for a decrease in detector gain due to a decreased gas pressure as the gas flow rate diminishes.

In order to investigate more fully the previously reported problem [8], concerning the need to continually adjust the anode potential over long operating times, a new lucite block was placed inside the detector chassid. However the lucite was not coated with aluminium paint and therefore the inner cylindrical wall was not in good electrical contact with the aluminium chassid. After mounting a sample which was grounded in the normal manner, it was found that the count rate
of the recorded Mössbauer spectrum gradually decreased over a period of about three hours by a factor of four. In fact, a fluctuating count rate was often observed. Turning off the anode potential for about ten minutes restored the count rate to its original higher value. The lucite block was then coated with a thin layer of aluminium paint. Under normal operating conditions, the original count rate was obtained and did not vary as a function of time. The observed effects can be explained in terms of a charge build up on the surfaces of the non-painted lucite block. This has the effect of altering the electric field in the region of the anode and eventually decreasing the gain of the detector. This effect can be partially compensated by increasing the anode potential.

The need to undertake low temperature CEMS measurements is illustrated by the spectra shown in figs. 3 and 4. In each case the project has involved the study of many samples at different temperatures using both electrons and X-rays. This necessitates the requirement of a detection system which is simple to construct and operate in order that several such systems can be used simultaneously. Fig. 3 shows the results of the corrosion products which form on weathering steel which has been subjected to a marine environment for five years.

The spectrum of fig. 3a recorded at 298 K is difficult to analyze accurately. Spectra recorded at high and low velocity ranges indicate that no high velocity peaks are present. The low velocity spectrum of fig. 3a which has been reproduced to match the same velocity range as fig. 3b, indicates the possibility of the presence of the α, β and γ phases of FeOOH. This is confirmed in the low temperature spectrum (fig. 2b), which shows the α-FeOOH component as the magnetically ordered sextet.

Fig. 4 shows the spectra of iron implanted polyethylene (1 × 10¹⁷ ⁵⁷Fe cm⁻²) recorded at 298 K and 100 K. These results form part of an investigation of the products formed in polymers implanted at different fluences with ⁵⁷Fe. The high fluence spectra indicate that at room temperature some superparamagnetic ordering is present due to small aggregates of iron atoms. As the temperature is decreased the superparamagnetic peaks become better resolved as a result of the slowing down of the magnetic fluctuations. (fig. 4b).

5. Conclusion

The increased use of conversion electron Mössbauer spectroscopy for the study of near surface phenomena has lead us to develop an easily constructed gas flow
proportional counter which is simple to operate between 100 K and 400 K. The system is inexpensive to build and several such systems can be simultaneously maintained. Once the counter is well sealed and the correct gas mixture is selected, the counter operates reliably and with good efficiency and signal-to-noise. For general operation of the detector, it is important to resolve the contribution of the resonantly emitted electrons from the background radiation and amplifier noise. This is best done by adjusting the gas flow rate, high voltage and amplifier gain while observing the pulse height spectrum. Although this is easy to undertake at room temperatures and above, the decreased detector gain at low temperature often results in the resonant signal being closely superimposed with the amplifier noise. This makes it difficult to set the lower level discriminator accurately. In fact unless a matched absorber is used (in our case 30% enriched Fe in Rh), the most efficient setting of the lower level discriminator is impossible. The matched absorber allows pulse height spectra to be easily recorded on and off resonance. At room temperature and above, all the gas mixtures studied could be used satisfactorily and gave good separation between the resonant electron peak and non-resonant background radiation. As the operating temperature was decreased, gases with low concentrations of methane were found to be unsatisfactory. At 100 K He/5% CO gave the best resolution. At this temperature it was necessary to increase the anode potential by about 200 V above its room temperature value and also to increase the gas flow in order to compensate for the lower gas multiplication factor. In designing the CEMS detector to operate at low temperatures, it was important to have the capability of operating at voltages up to at least 1300 V without the initiation of spurious discharges, yet maintain a small sensitive volume in order to obtain a high signal-to-noise ratio.

References