CHAPTER II

THE USE OF POSITRONS FOR THE STUDY IN MATERIALS

2.1 Introduction

This chapter provides information on the interaction of positron in materials, the characteristics of positron/electron annihilation (PA), and the methods for measuring PA focusing on the Doppler-broadened positron annihilation (DBPA) technique which rely on the shape profile of an annihilation line as a quantitative measurement. Finally, the applications of PA in materials will be provided.

2.2 Interaction of positron annihilation (PA) in materials

In 1930, positron was discovered for the first time by Dirac [2]. It is an antiparticle of electron with positive charge and when interacts with an electron, a positron/electron pair is formed, a positronium, which is unstable and will annihilate. The result of annihilation process is two photons, each one has an energy of 511 keV, emitted from the center of the mass of the pair at approximate 180° to one another. The annihilation process is shown in Figure 2.1.

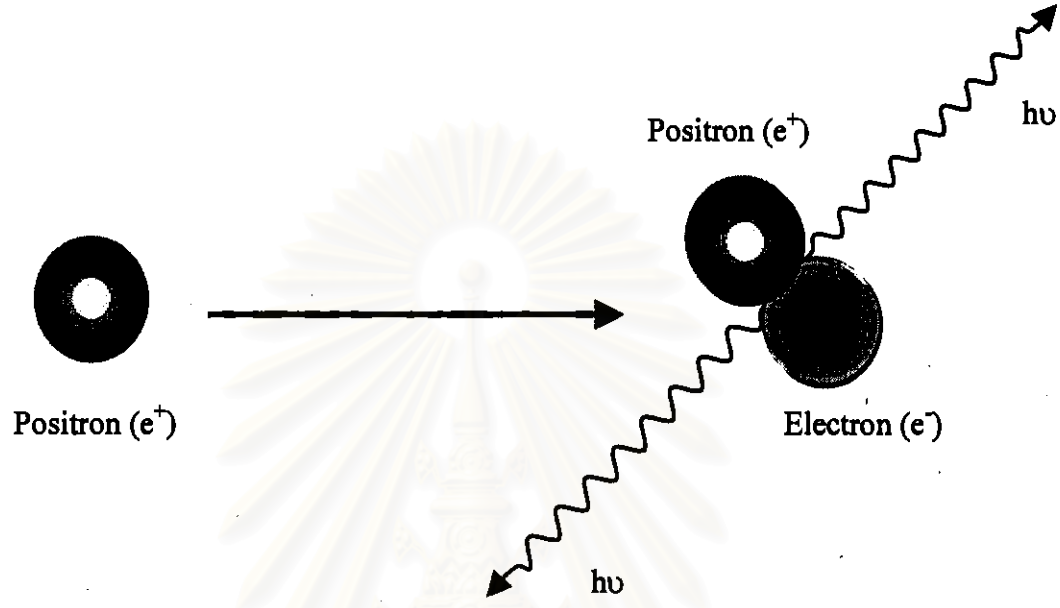


Figure 2.1 The annihilation process.

A very slight departure from 180° is directly proportional to the transverse component of the momentum of the photon pair, and the momenta of electron involved in such collisions can thus be calculated from geometry and intensity of gamma rays, Figure 2.2. The characteristic of PA which are related to the electron distribution in materials [3], allowed this technique to become a non-destructive evaluation (NDE) technique in solid target at level well below the resolution of most other techniques. Not only this technique has excellent resolution but also it is sensitive to minute changes and can be used as a tool to monitor the changes either during manufacturing or during the lifetime of parts.

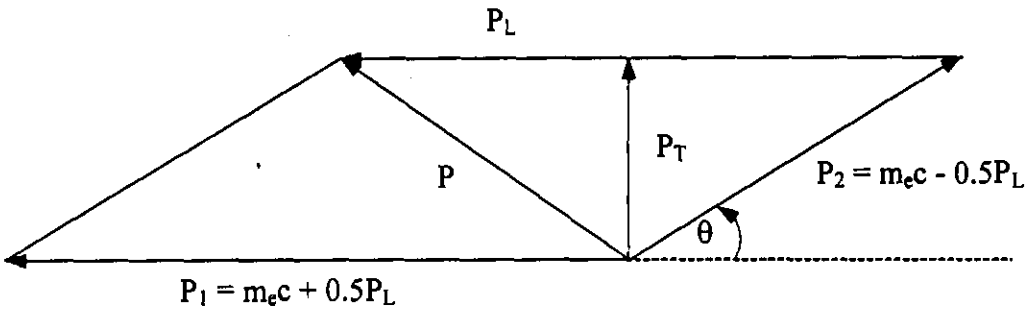


Figure 2.2 Momentum conservation of the two γ-ray positron annihilation. P is the momentum of the positron/electron pair, and P_L and P_T the longitudinal and transverse components respectively. [7]

PA was applied for the first time to evaluate the imperfection in crystal lattice, such as dislocations, vacancies etc., in Ni and its alloys samples [4]. Figure 2.3 shows the angular distribution spectra for Ni and its alloys in annealed and deformed states. This experiment demonstrated that the electron energy spectrum is significantly modified at deformation. At present, PA has been used as a non-destructive testing (NDT) technique in materials by two main methods of measurement: lifetime and momentum.

2.3 The category of PA measurement

The two main methods used for the experimental investigation of PA are as follows: [3]

1. Lifetime measurement.
2. Momentum measurement: this can be either angular correlation or Doppler-broadened measurement.

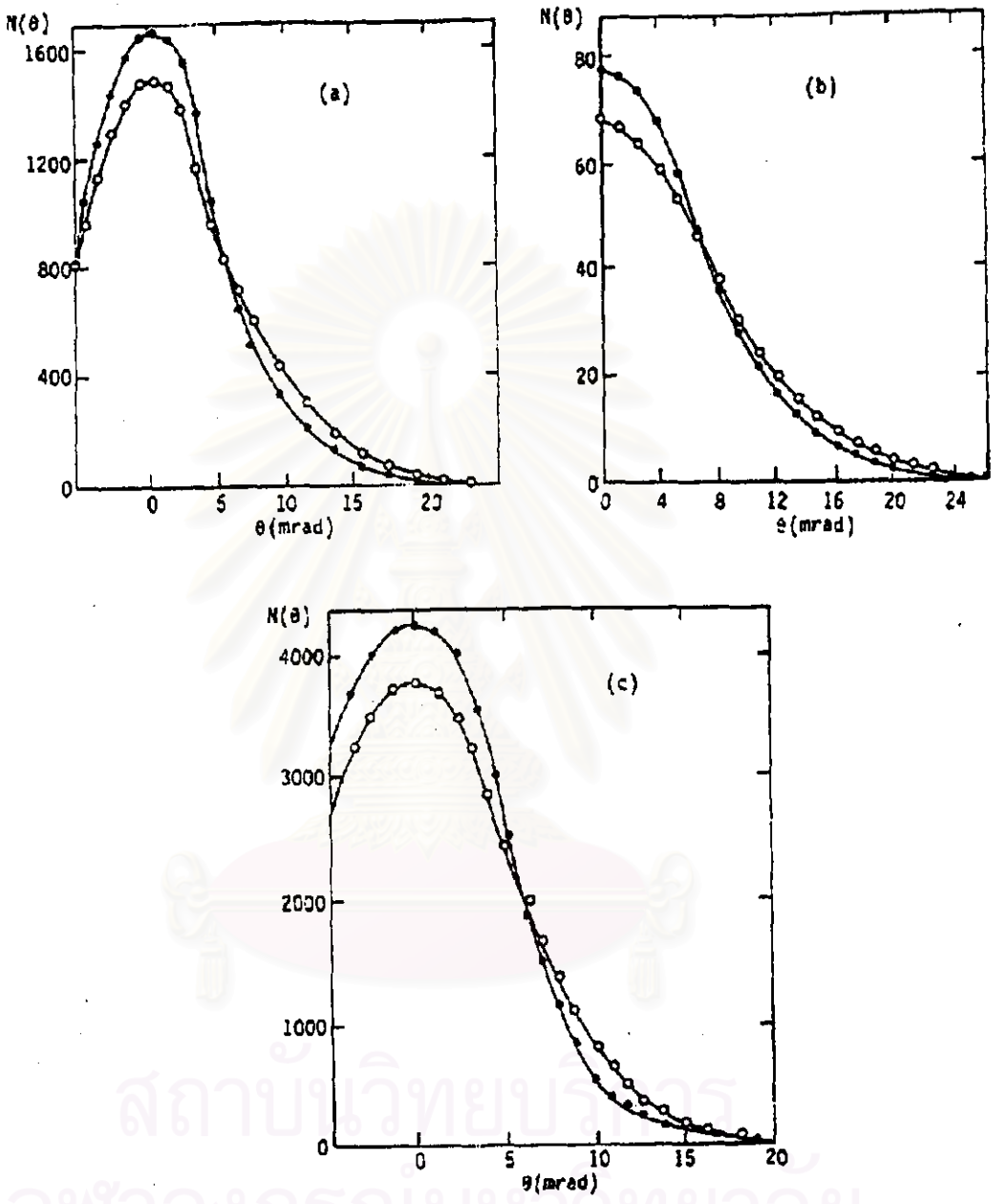


Figure 2.3 Angular distribution spectra for annealed (o) and deformed (•):

(a) Ni, (b) Ni + 62%Fe and (c) Fe + 1.08 at%Al. [4]

Lifetime measurement: the lifetime of positron can be measured as the time decay between the birth photons and the death photons, Figure 2.4. The birth photon may be obtained from prompt gamma rays emitted from the positron source almost simultaneously with the positrons [5]. The 1.274 MeV gamma rays from Na^{22} are proposed to be these photons. The death photons are always provided by the annihilation gamma rays. Basically, positrons become rapidly thermalized in a metal in a few picoseconds (ps) and are trapped at the defects. The lifetime of thermalized positrons depends on the average electron density at the positron-trapped site. Thus, lifetime can be used to identify the defects [6] such as: the lifetime of vacancy, edge dislocation and screw dislocation in iron were found to be 175 ps, 165 ± 2 ps and 142 ± 5 ps respectively. The basic circuit of an apparatus is shown in Figure 2.5. The disadvantages of this measurement are the complexity of the set up, requiring fast electronic apparatus and precision in the measurement.

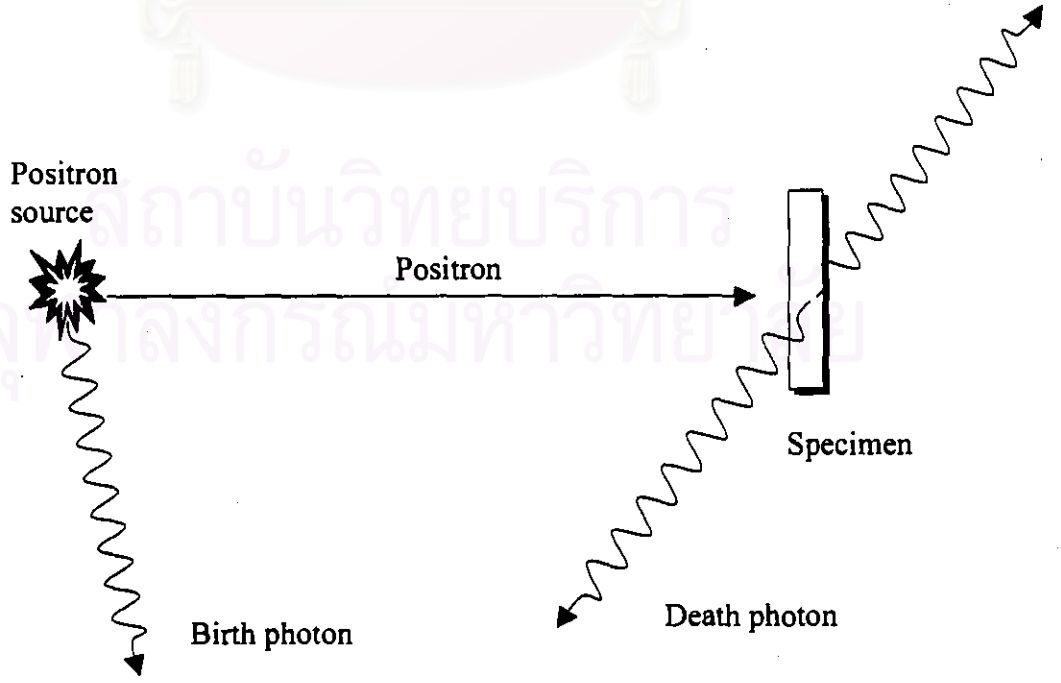


Figure 2.4 Definition of the birth and death photons. [5]

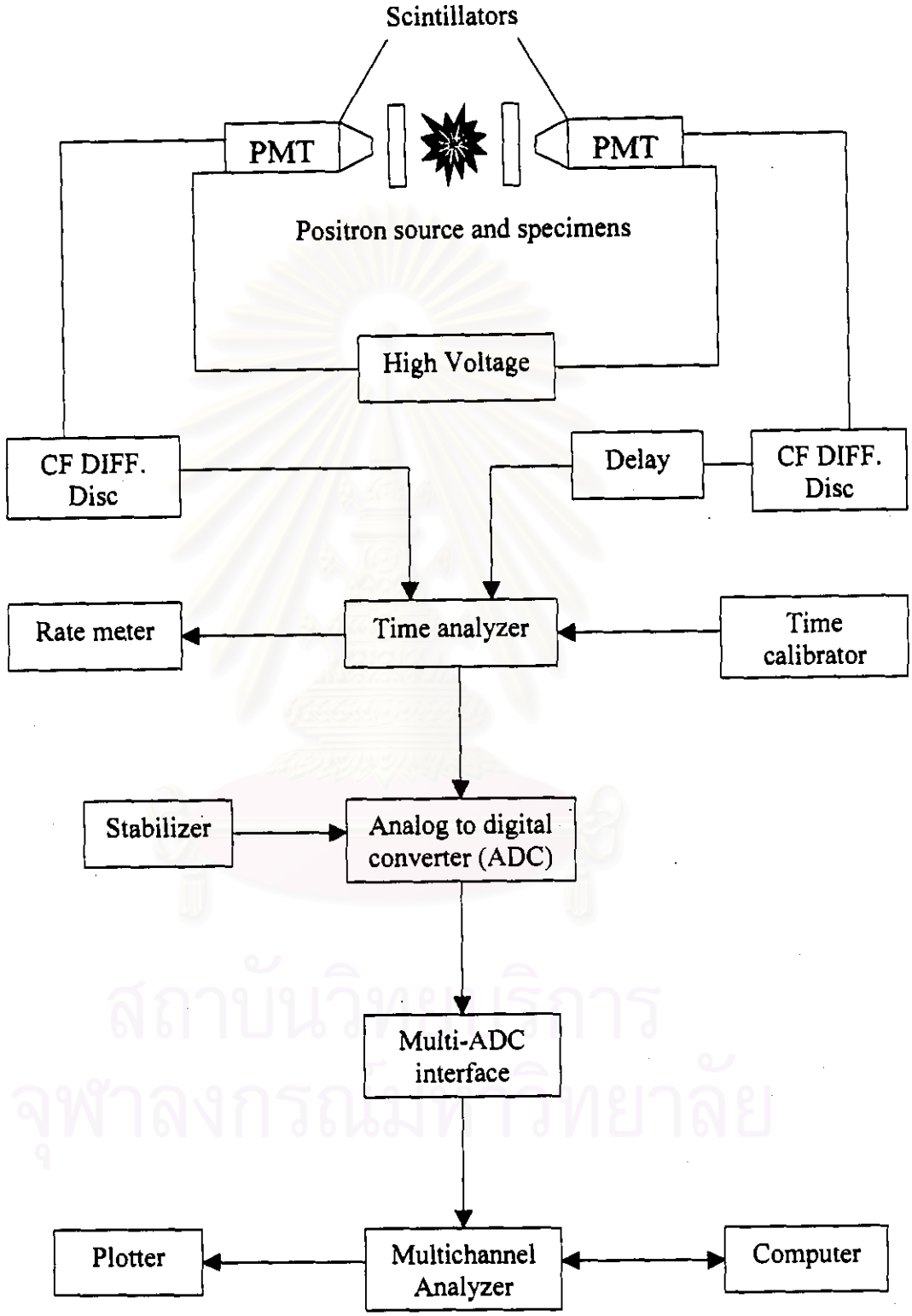
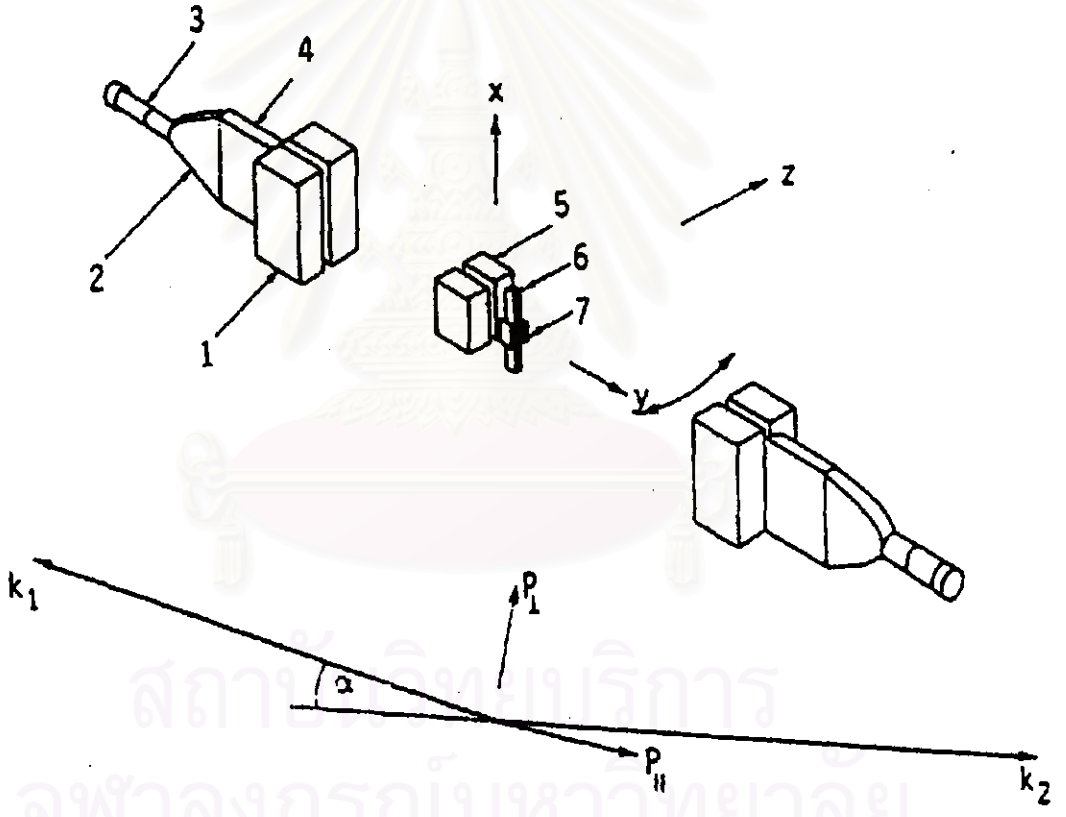


Figure 2.5 The basic circuit of an apparatus for lifetime measurement.

Angular correlation measurement: theoretically, the energy of each annihilation gamma ray is exactly 511 keV, and the two gamma rays are emitted in exactly opposite direction. However, two gamma rays are generally not emitted at exactly 180° [7]. The angle (θ) deviated from 180° contains the information about the momentum distribution of the electron. The experimental set up of this measurement is shown in Figure 2.6. The experimental set up requires restrictive geometry.



1: Slit

2: Light pipe

3: Photomultiplier

4: Scintillator

5: Supplementary slit

6. Sample

7. Positron source

Figure 2.6 The schematic arrangement of angular correlation measurement. [2]

Doppler-broadened measurement: this measurement based on the motion of positron/electron pair before annihilation causes a Doppler shift of two gamma rays. The energy shift ($\Delta\varepsilon$) which reflects the momentum distribution of electrons can be detected by high energy resolution detector because $\Delta\varepsilon$ is very small. Figure 2.7 shows the block diagram of this measurement which consists of a positron source, investigated specimens, a semi-conductor detector, the gamma ray detection system and a computer unit.

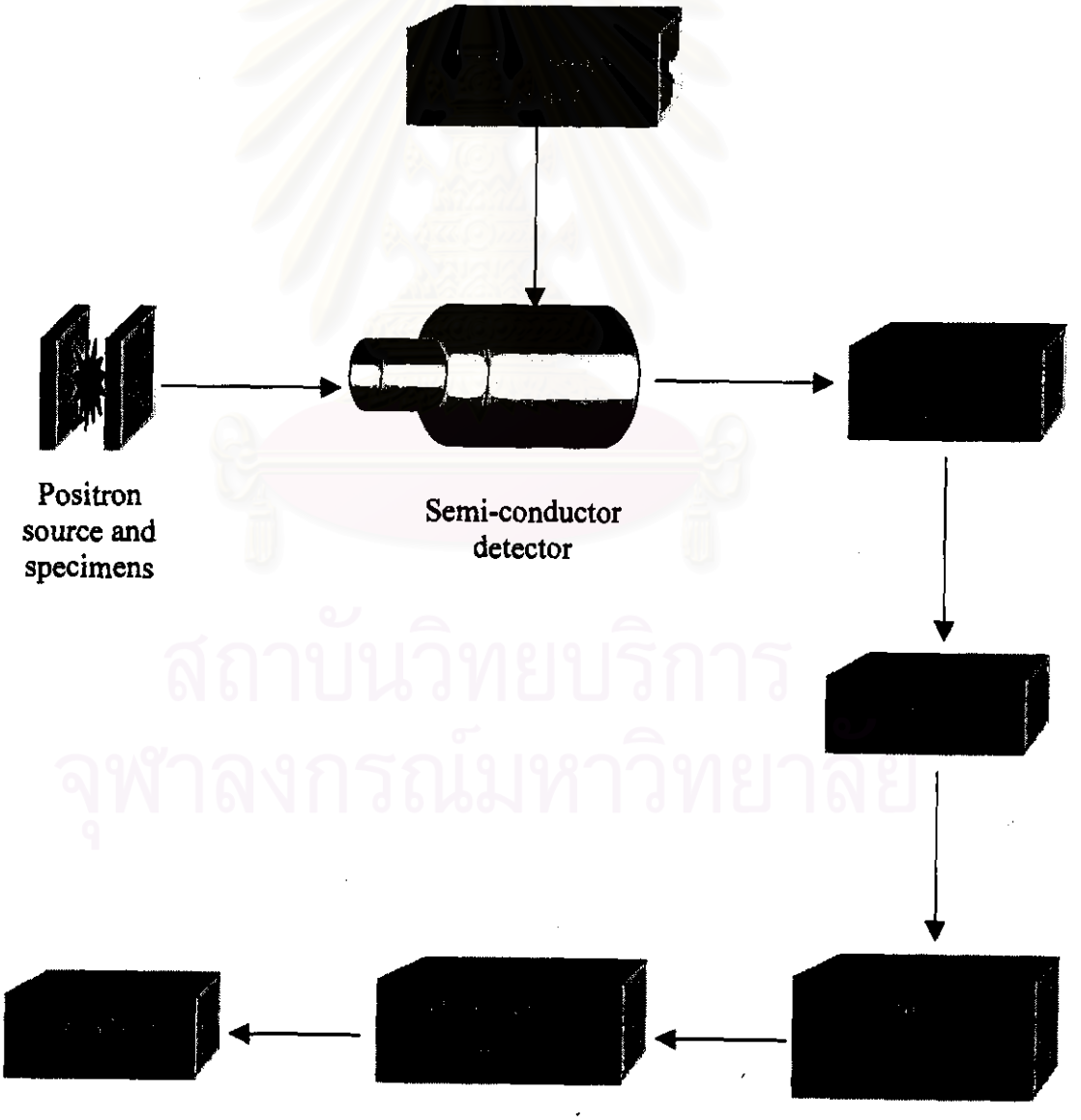


Figure 2.7 The schematic diagram of DBPA measurement system.

The three modes of PA measurements, lifetime, angular correlation and Doppler-broadened measurements, provide the information about electron distribution and density. Nevertheless, the experimental set up of the lifetime and angular correlation measurements are complex, require the large area and fast electronic apparatus. The simplest positron annihilation measurement and one of the most sensitive techniques is Doppler-broadened positron annihilation (DBPA) measurement [3] which offers several advantages over angular correlation measurement [8] being lower source strength requirement, shorter data collection time and less restrictive geometric requirement. The conventional lifetime and angular correlation technique with their low counting rates don't compete with DBPA in the respect. Not only several advantages of DBPA technique but also the equipment of DBPA set up can be obtained from this department, thus we propose to use this technique for this thesis.

2.4 Doppler-broadened positron annihilation (DBPA) spectroscopy

The recent studies in solid metal suggest that positron may tend to annihilate in low density regions around dislocations or vacancies [9] and the calculations by Hodges [10] and measurements of MacKenzie et al. [1] demonstrated that both vacancies and dislocations in metals are able to trap positrons and thereby cause them to annihilate with a different electron distribution than in a defect-free lattice. As positrons entered and trapped at lattice defects, they combine with electrons and annihilate yielding gamma rays and exhibiting a Doppler-broadening around its mean

value of 511 keV. The signals of DBPA measurement are different in perfect and imperfect crystals, annihilation between the positron and slow electron at defect causes the 511 keV line to take a narrow shape, while an annihilation with an electron from a perfect lattice produces a 511 keV line with a broadened shape, see Figure 2.8, and these signals can be observed by using semi-conductor detector. However, the resolution of DBPA lineshape is insufficient for estimation of momentum density of electrons involved in collision so the parameters such as S, L, R, W and D were introduced for estimation of electron momentum density.

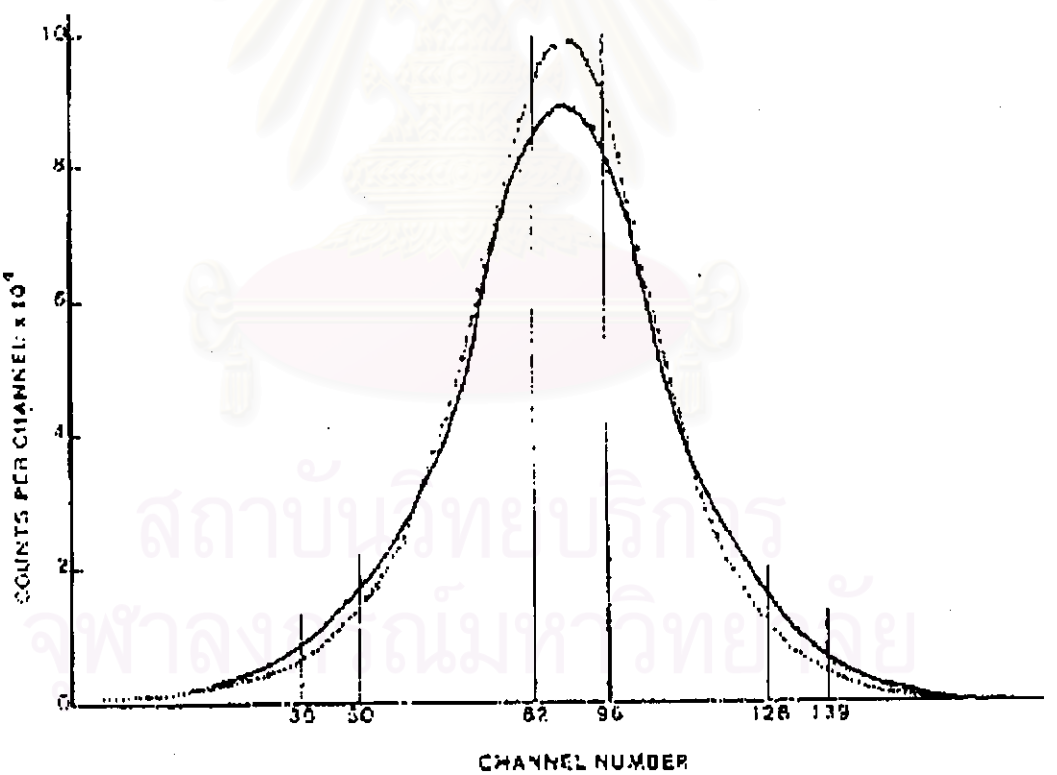


Figure 2.8 The Doppler-broadened positron annihilation spectroscopy of annealed (—) and heavily deformed (---)copper.

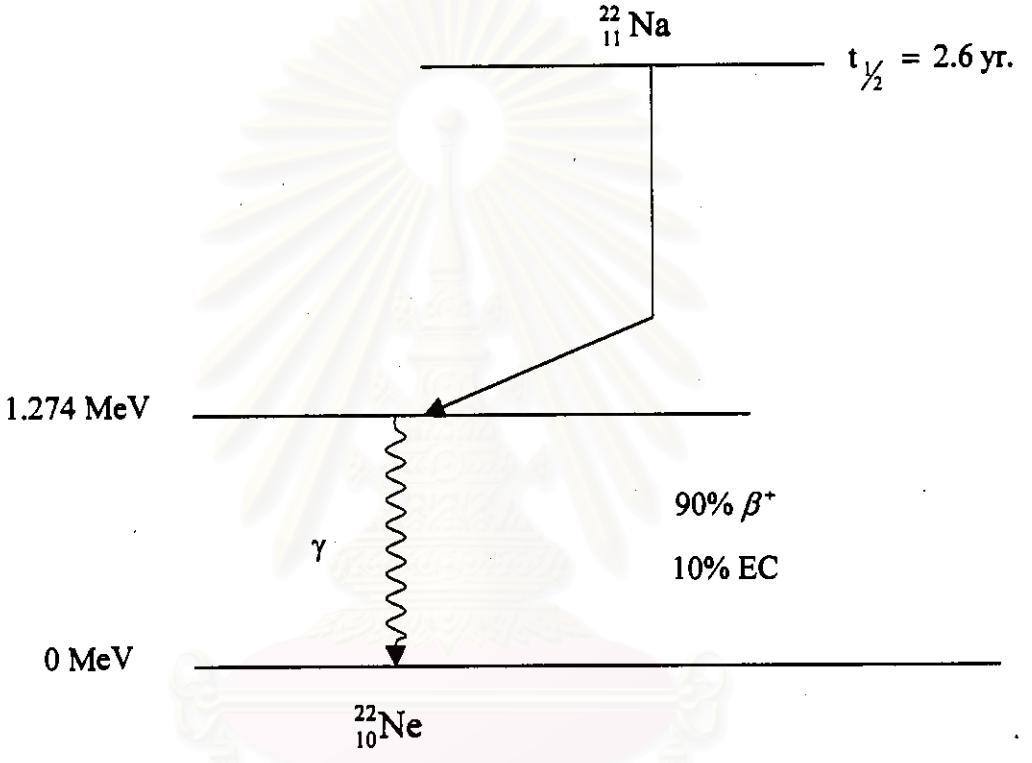
2.4.1 DBPA measurement system

A system for measuring the DBPA spectroscopy as shown in Figure2.7 consists of a positron source sandwiched between investigated specimens, a semi-conductor detector, a gamma ray detection system and a computer unit to process and collect information. The important properties of positron sources are a high rate of positron radiation and sufficient positron energy to leave the source and enter the investigated specimens. There are a large number of positron sources suitable for the experiments, e.g. Na^{22}, Co^{55}, Ni^{57}, Co^{58}, Cu^{64}, Ge^{68} and Nb^{90}. Nevertheless, a commonly used source is Na^{22} [7] and will be discussed in details below.

The isotope Na^{22} has become the standard source for positron annihilation because it has a positron branching ratio of 90% and has a conveniently long source lifetime ($t_{1/2}$ = 2.6 yr). In addition, the Na^{22} source has other important properties, it emits 1274 keV gamma ray after positron decay which can be used as a birth photon in lifetime spectroscopy. The other reason is that the source can be applied in many researches because it can be used as a solution or solid source. The decay scheme of Na^{22} is shown in Figure 2.9.

For the measurement of DBPA spectroscopy, the gamma detector with very high energy resolution is required. Since the energy shift from 511 keV peak is very small, a semiconductor detector is thus recommended for this measurement. Because of the shape of DBPA spectrum must be quantifiably described and the resolution of the lineshape of DBPA measurement is generally insufficient for

evaluating the shape profile of annihilation line reflecting the state of microstructures inherent in materials, many parameters such as S, L, R, W and D were thus introduced to solve this problem.



γ = 1.274 MeV γ (100%) annihilation radiation.

Figure 2.9 The decay scheme of Na^{22}.

The S parameter, introduced by MacKenzie [11], was defined as a ratio between the centroid area (n) and the total peak area (N), $S = \frac{n}{N}$. Figure 2.10 shows the definition of area for calculation of parameters.

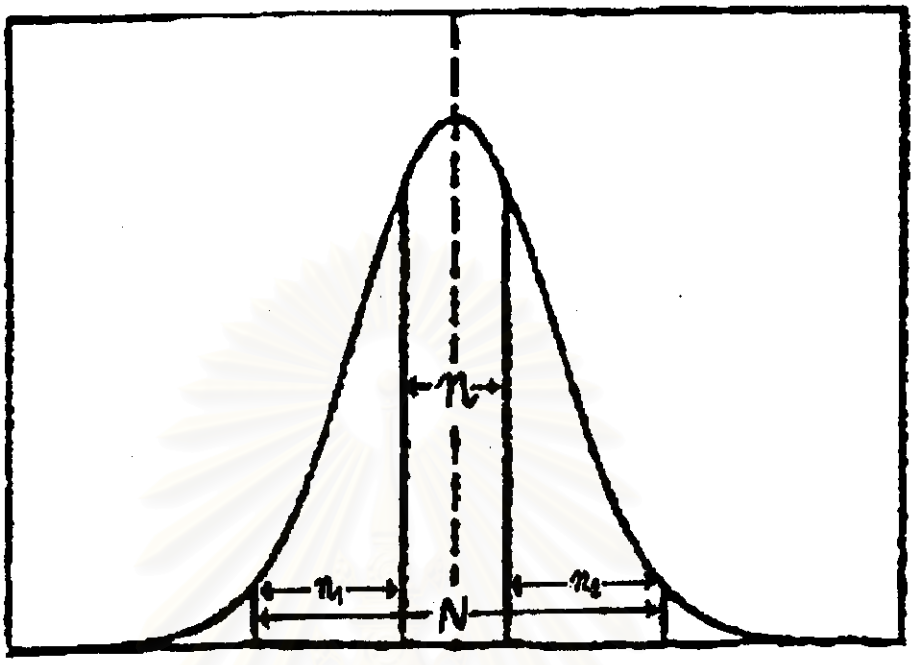


Figure 2.10 The definition of area for calculation of the parameters.

This is the most popular parameter used to characterized annihilation spectrum. However, MacKenzie et al. [12] realized that the S parameter only crudely reflects the fraction of the total annihilation that occur with valance electrons, it increases as the defect density in crystalline solid increases and more positrons are trapped. Conversely, the density in the wing regions of the peak is depleted as the annihilation with core electron diminish. A parameter, L was thus introduced and defined to emphasize the different between the trap sites of positrons [12]. L is the ratio between the centroid area (n) and symmetrically placed groups in the wings of the spectrum (n_1 and n_2). From the figure 2.10, L is defined as:

$$L = \frac{n}{n_1 + n_2} = \frac{S}{W} , \qquad (2.1)$$

where a narrow n and a component ($n_1 + n_2$) are mainly associated with annihilation with valance electrons and core electron, respectively. The wing parameter [11], W, is used for calculation of L parameter can be defined as a ratio two-side area of the peak and total area. The W value is expressed by the following equation.

$$W = \frac{n_1 + n_2}{N} \tag{2.2}$$

Not only L parameter can be used to identify the positron trapped site but also to evaluate the concentration of deformation by measuring this lineshape parameter for a perfect and deformed specimens.

Another parameter which based on two-state trapping sites is R parameter. This is a defect-specific parameter was proposed for the first in 1975 by Mantl and Triftshauser [13]. R value can be calculated by this equation.

$$R = \left[\frac{S_d - S_f}{W_d - W_f} \right], \tag{2.3}$$

where d and f are the sites of positrons are trapped in the defects and in the trap-free bulk, respectively. The changes of R can be used to indicate the changes in dominant trap site during annealing and R values can be used to identify the different defects, for example, Park et al. [14] identified R value for edge dislocation to be 1.8. However, this parameter has not been extensively used in the literature. One difficulty arises because there is no agreement on how to define the S value or wing parameter in DBPA spectrum. Although, the justification for the choice has been published but it is not sufficient to report the number of channels used.

If combination of function of the two parameters, S and W, is used. The correlation between centroid and the summation of two-side area of spectrum must be recognized in calculating the variance of the new function, D parameter. This parameter was introduced by Campbell [11] and defined as:

$$D = S - W \tag{2.4}$$

This parameter offers the sensitivity that is only marginally better than S, but the dependence of sensitivity on channel limits is much weaker than S and W parameters. Although, there are many parameters proposed for evaluating the shape profile of DBPA spectrum, all parameters were essentially a mathematical manipulation of the centroid and the wing regions which are believed to be related to valance and core electrons, respectively. Nevertheless the S parameter is much more widely used because it only needs the definition of the centroid region while the others need wing area definition which is more vaguely defined.

2.4.2 S parameter

The S parameter, introduced by MacKenzie et al. [11], is widely used to evaluate the shape profile of an annihilation spectrum reflecting the state of microstructure inherent in the solid. The S parameter is defined as a ratio of the centroid area (n) to the total area under curve (N). From Figure 2.10, S value can be expressed as follow:

$$S = \frac{n}{N} \ , \tag{2.5}$$

However, there is no established criterion to define the centroid of the spectra [15], therefore a comparison of absolute values of S obtained by different investigators is not possible. Generally, the centroid area is fixed as the area between $511 \pm \Delta\varepsilon$ keV, $\Delta\varepsilon$ is the energy shift depending on the materials being investigated. It should be noted that the selected value of $\Delta\varepsilon$ has never been clarified in most of the literature and the value of 1 keV was cited in a few occasions [8]. The choice of $\Delta\varepsilon$ can greatly affect the value of S parameter and thus, was found to lack of its clear physical and/or statistical meaning. Furthermore, S values are affected by many variables such as: counting rate, temperature, humidity, geometry, instrumental instability, liquid nitrogen level etc., causing instability of the lineshape affecting the accuracy of S parameter. Thus, several correction and/or compensation techniques have been proposed to keep the S parameter errors low and providing better statistical confidence. The statistic of S parameter is concerned because the change of S value is only in order of a few percent as defects change by almost 1-2 order magnitudes. The correction and/or compensation technique which proposed by several investigators for correction of the S values mainly focused on counting rate variation and instrumental stability.

Zecca et al. [16] proposed two methods for correction and/or compensation of S values which associated with counting-rate variation. The first method can be applied by setting the windows of centroid area and total peak area referring to energy scale rather than to a channel number position. This important is greater if large channel widths are used. This method successfully corrected the line-shift error and the line-broadening error on the S parameter. The other method used a

movable gamma source. A feed-back circuit moves the gamma source so as to keep the total count rate constant. Dorikens-Vanpraet [17] had shown that this method could overcompensate or undercompensate the S value, according the selection of gamma source. The perfect compensation will be achieved when annihilation gamma ray is substituted by gamma ray with nearly the 511 keV energy. It was found that the use of Cs^{137} gives the good compensation. Figure 2.11 shows the S variation with different gamma source in a moveable gamma source method. However, this method has been judged to be too difficult to implement.

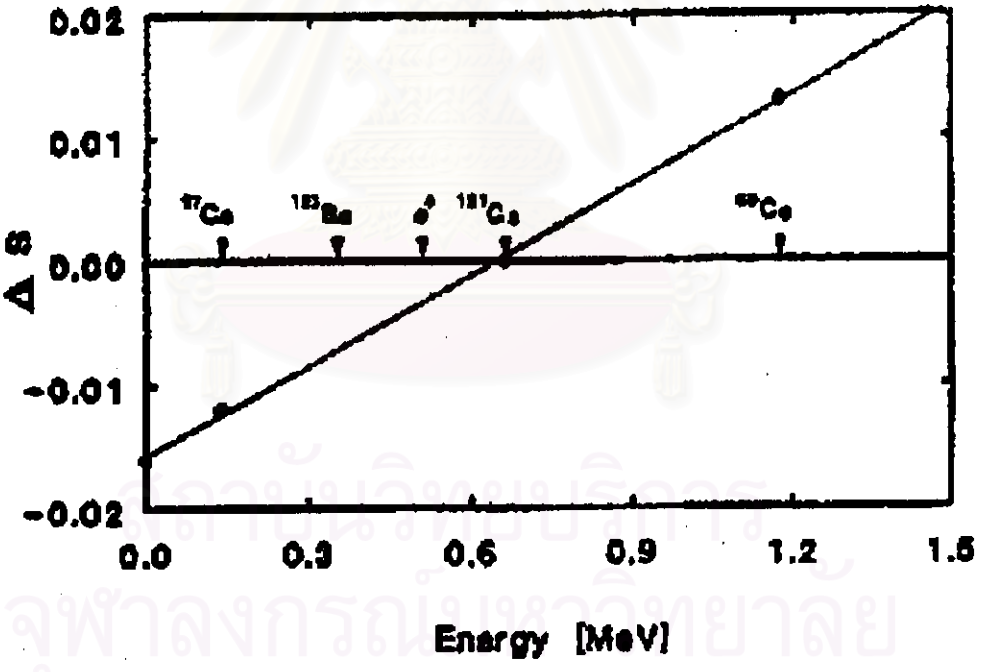


Figure 2.11 The variation of S parameter with different moveable gamma source. [16]

The problem of instrumental instability effects on S value has been addressed by several investigators using a reference gamma source with an energy peak which is close to but does not overlap with the 511 keV annihilation peak and

some mathematical analysis [18-19] and microspectrum data collection method [9]. The details of these methods vary, but the same basic idea is to correct or compensate the effects of instrumental instability on S value. Kerr et al. [18] had proposed the method to correct the S error caused by the change of energy resolution during the experiments. This change can be observed by simultaneously recording the reference spectrum which produced from another gamma source with having its energy closed to the annihilation spectrum. In addition, the analytical correction formula which was derived under the approximation of a Gaussian shape of DBPA and reference spectrum was proposed to correct the S values. Kerr's formula was shown in equation 2.6.

$$S_A^{\circ} = S_A - \Delta S_R \left[\left(\frac{\sigma_R^3 \, \Sigma_A}{\sigma_A^3 \, \Sigma_R} \right) \exp \left(\frac{\Sigma_R^2}{2\sigma_R^2} - \frac{\Sigma_A^2}{2\sigma_A^2} \right) \right] , \qquad (2.6)$$

where S_A° and S_A are the corrected and measure S values of annihilation spectrum respectively. ΔS_R is the difference between experimental and ideal S value of reference spectrum. The standard deviation (σ) obtained from the full width at the half maximum of spectrum. Σ is the channel limit employed for the centroid area in the S parameter. The application of equation of 2.6 to correct S parameter of 478 keV Be^7 gamma ray spectrum and DBPA spectrum in indium specimens at constant temperature and pressure showed that this equation could be used to correct the S values in Figure 2.12.

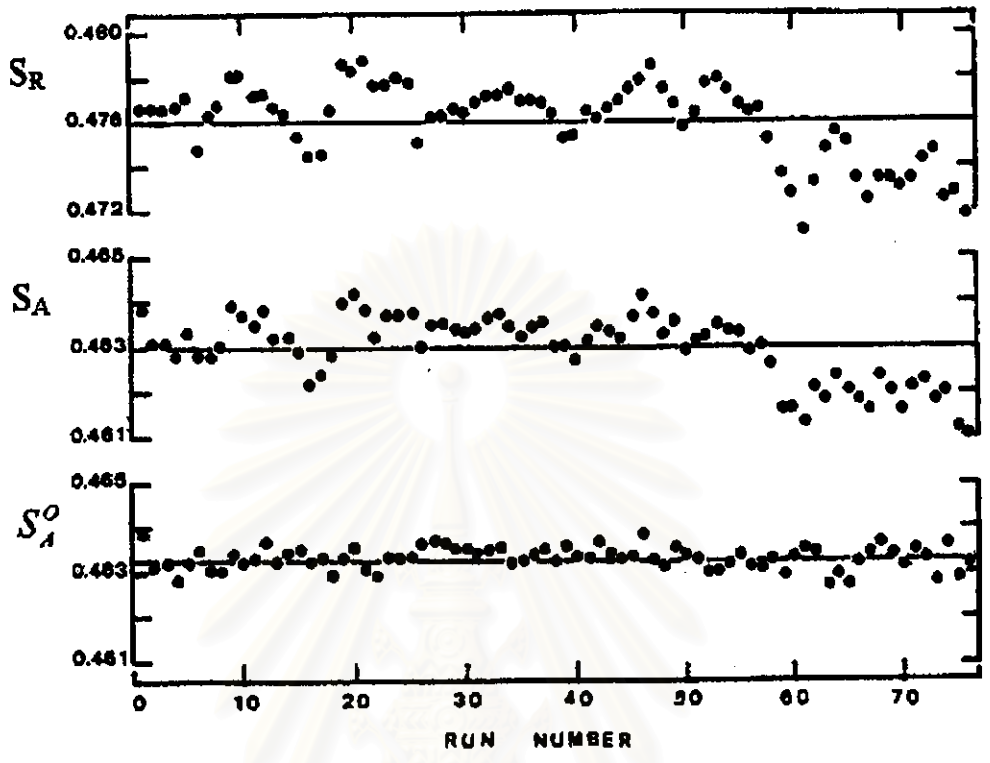


Figure 2.12 S parameter for a Be^7 reference curve (S_R), a Doppler-broadened Na^{22} in indium curve (S_A) and the corrected Doppler-broadened curve (S_A^*). [18]

Campbell and Schulte [19] proposed the mathematical formula to reduce S error caused by instrumental instability by using the correlation between changes in the reference and annihilation spectrum. Campbell proposed equation 2.7 to correct the S value.

$$S_A^o = S_A + \frac{dS_A}{dS_R}\Delta S_R \qquad (2.7)$$

where $\frac{dS_A}{dS_R}$ is defined as coefficient obtained from the slope of the relationship between a measured S parameter of annihilation and reference spectra.

Another investigator [8] has proposed an alternative method for reducing the effects of instrumental instability. The microspectrum data collection method was proposed by Fluss and Smedskjaer [20] to improve the resolution of DBPA technique by reducing S error via collection of the energy spectrum for a short time (~200 seconds) in order to reduce the effects of the non-linear instability. This technique also involves the calculation of the centroid distribution. These two steps were repeated until five such distributions were obtained. Next, the five isolated spectra were aligned so as to have a common centroid and then are summed to produce a signal spectrum which is increasing the counts so the statistical counting errors are reduced with approximately five times as many counts as any single small spectrum.

Despite many efforts by several investigators to improve the accuracy of S parameter, no standard correction/compensation technique for analyzing the S parameter has ever been established. This may be due to the specific nature of experimental set up and arrangements. Furthermore, no criterion for $\Delta\varepsilon$ has ever been set for evaluating the S value making it impossible for experimental results to be directly compared and benchmarked. Thus, the development of DBPA spectroscopy for this thesis is specially focused on developing electronics unit to stabilize annihilation line and techniques to obtain and analyze the S parameter with high degree of credibility.

2.5 Applications of DBPA spectroscopy in materials science

DBPA technique has been applied in many researches to study different type of defects [21-27]. Recently, its applications have been extended to commercial materials to investigate their microstructures making the technique an invaluable non-destructive evaluation at the atomic level.

It was the research group at the University of Guelp led by MacKenzie [28] first used DBPA spectroscopy in characterizing defects in metals. They applied this technique [1] to measure the percentage of positron trapped by dislocations in 99.999% copper and commercial aluminum alloy (6061). The percentage of trapping and the sample hardness tend to show a linear function with deformations on logarithmic scale, Fig 1.2. They concluded that DBPA technique is completely non-destructive and therefore can be used in many applications as a quantitative tool for the measurement of dislocation density.

Logar et al. [29] used lifetime and DBPA spectroscopy to investigate the vacancy-life defects induced by structural and radiation in NiAl. The intermetallic compound, NiAl, has been studied for more than two decades due to its attractive high-temperature properties. In spite of the fact that this kind of vacancy defects perform an important role in material characteristics, not very much is known about the behavior of vacancies or vacancy-type free volume. Preliminary results were found that the lifetimes of the annealed samples confirm that defects, most probably vacancies and vacancies complexes, are of structural type or quenched-in during the

production of samples. While S parameter of proton irradiated sample demonstrated the decrease of irradiation induced vacancy-like defects. Figure 2.13 shows the variation lifetime and the S parameter as a function of the annealing temperature for the proton irradiated as well as the unirradiated off-stoichiometric samples.

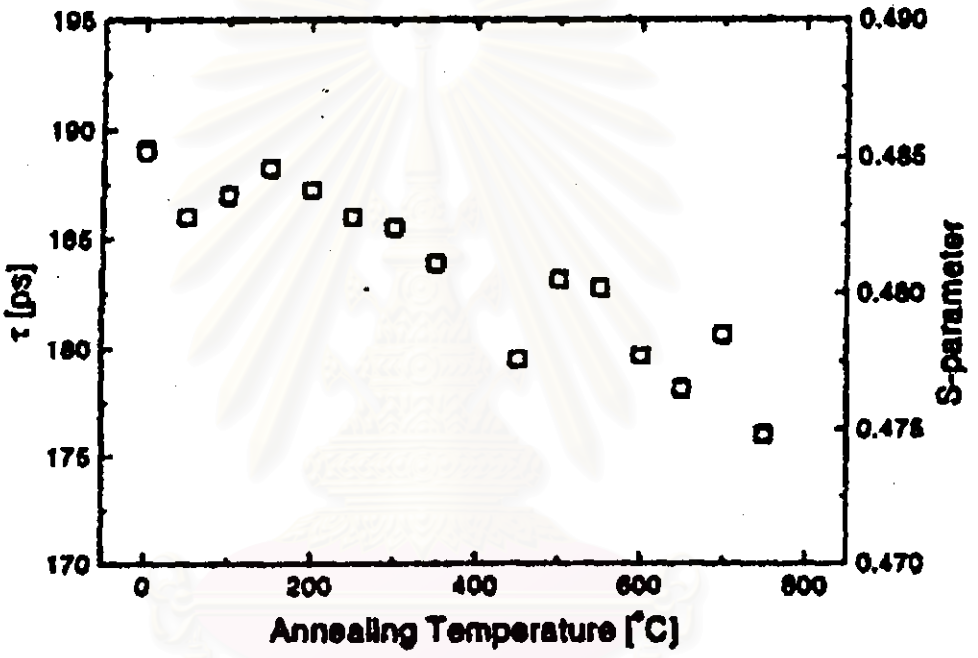


Figure 2.13 The variation lifetime and S parameter as a function of the annealing temperature for the proton irradiation samples [29].

Dull et al. [30] employed DBPA spectroscopy to study the corrosive breakdown of TiO_2 passive film on Ti. Passive oxides films protect a reactive metal surface from its environment and the breakdown of these films results in corrosion of the metal. The most detailed theory of passive film growth and breakdown in contact with reactive environments is the Point Defect Model (PDM) based on the assumption that passivity breakdown initiates when metal cation vacancies within the film formed

at the surface. Hence, detection and characterization of cation vacancies within the film and interface are essential. They concluded that the trend of S value, Figure 2.14 shows the result of the study for three polarization voltages, is in accord with the PDM which predicts that in the initiation stage of passivity breakdown cation vacancies are first generated at the solution/film interface and diffuse to the film/metal surface

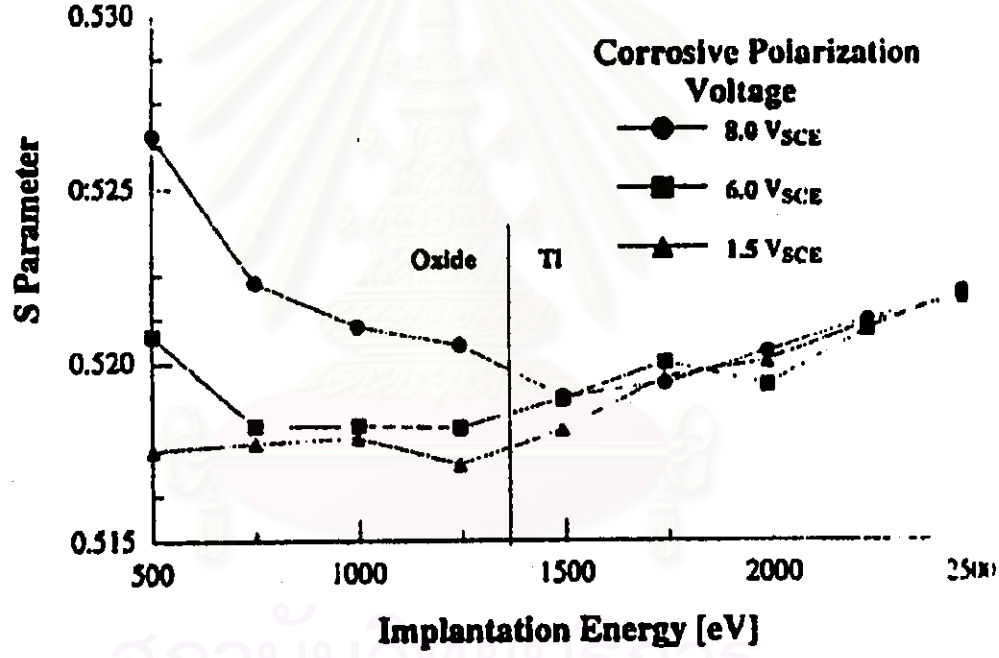
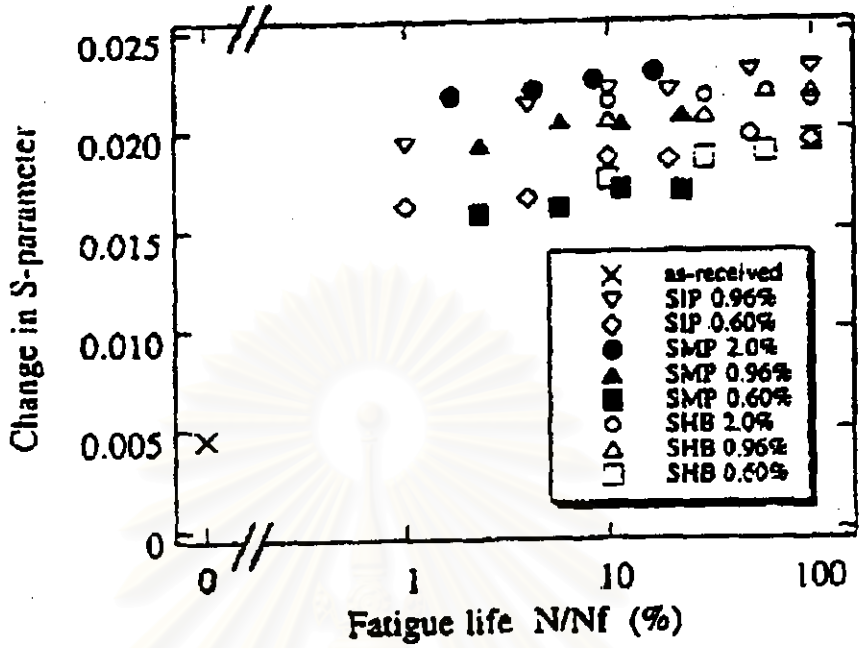


Figure 2.14 The oxide films form on titanium foils and corroded at various polarization potentials. [30]

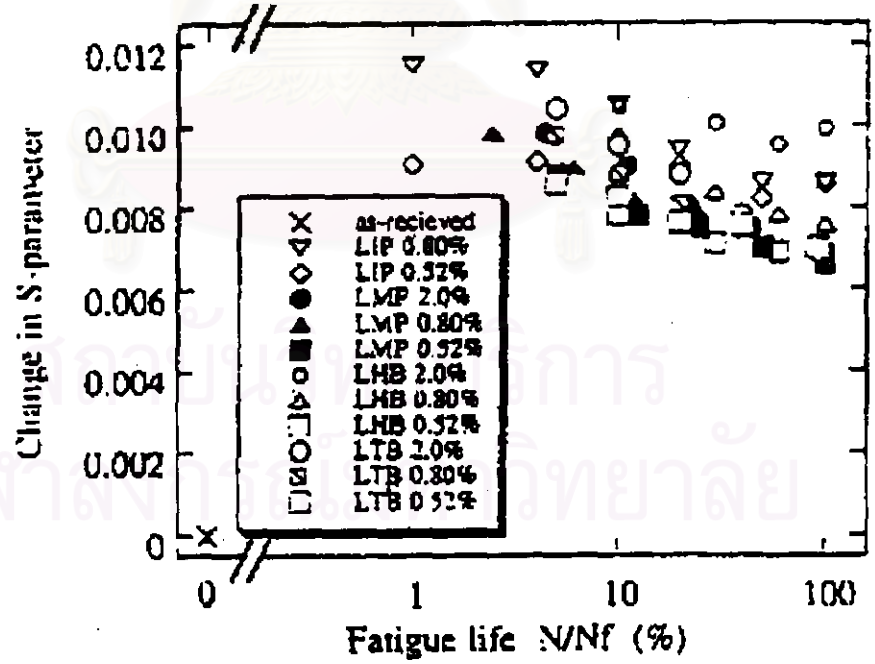
Maeda et al. [31] used the DBPA technique to analyze fatigue damage of 316 and SA 508 (0.67 at% Mo, 0.87 at% Ni, 36 at%Cr, 0.7 at% Mn) low alloy steels used in nuclear power plant. The fatigue damage is well known as one of the failure causes in many structural components. The fatigue damage process in metals is divided into

the following three stages: crack initiation, crack propagation and failure. The condition for crack initiated and propagated rate are strongly affected by the microstructure. To make a reliable evaluation of nuclear power plant life, it is necessary to know that the correlation between the microstructural change during fatigue deformation and process of crack initiation. The DBPA technique was found to be sensitive in the early fatigue life, but showed little sensitivity in later stages of the fatigue life in both alloys tested, Figure 2.15 shows the changes of S value in both alloys.

Through some of these researches, it can be clearly seen that the DBPA technique has proven to be an invaluable tool to probe into materials microstructures and may be used to provide us with an insight into structure/property relationship without disturbing materials integrity. Thus thesis attempts to extend the application of the DBPA technique to evaluate the sensitization condition of stainless steels. The sensitization refers to the breakdown in corrosion resistance which may occur if unstabilized austenitic stainless steels are slowly cooled from the solution anneal temperature (~ 1100°C) or are reheated in the temperature range 600 to 750°C [32].



(a)



(b)

Figure 2.15 Change in S parameter in type 316 stainless steels (a) and in SA508 low alloy steel (b) as a fraction of the fatigue life. [31]