

## CHAPTER 2

## BACKGROUND

Sintering in a Powder Metallurgy Method 1-16

From the ASTM definition, sintering is explained as the bonding of adjacent surfaces of particles in a mass of metal powders or a compact by heating. The sintering process can be classified into two types :

1. Solid phase sintering
2. Liquid phase sintering

Solid phase sintering is the process by which metal powders are transformed into dense and coherent solids at temperatures below their melting points. When powders of metals, either in a loose form or previously compacted by the application of pressure, are heated at sufficiently high temperatures, the particles of powder weld together, the bulk dimensions of the specimen decrease, and the resulting somewhat porous mass acquires a certain mechanical strength. The variables governing the process are temperature, sintering time, size, shape and the surface of the powder particles, nature and pressure of the gas surrounding the powder during sintering, and pressure used in compacting the powder before sintering. Sintering process can be divided into two parts, the first part deals with bonding of particles so that a point of contact becomes an area of contact

with a certain typical geometrical configuration. When this process has advanced to a certain degree, the cavities between particles gradually close and tend to become spherical. The second process is a gradual decrease in the size of the pores, resulting in a shrinkage of the bulk dimension of the compact. It is believed that surface tension or capillary force acts as the driving force and is responsible for bonding as well as reduction in pore size. The theoretical as well as experimental results indicate that the bonding of metallic particles and the consequent increase in contact area are due mostly to volume diffusion flow.

In bonding of particles, there are five different mechanisms by which the material can be transferred from the sphere into the narrow wedge-shaped cavity, namely viscous or plastic flow, volume diffusion, surface diffusion, grain-boundary diffusion, and evaporation-condensation. The first three mechanisms are based on a series of assumptions that the atomic mechanism for both volume diffusion and viscous flow is essentially a vacancy mechanism, in which the atoms move by jumping into vacant lattice sites; while in surface diffusion flow, a vacancy concentration gradient is also assumed to exist. The difference between volume diffusion and viscous flow is that for viscous flow a stress must be applied in order to move the vacancies throughout the solid, whereas for displacing material by volume diffusion a vacancy gradient must be established.

It is easy to visualize that surface tension may cause the material to flow and make possible the volume diffusion flow.

In the volume diffusion flow the surface tension must create a vacancy gradient to make this mechanism possible. Because near the interface between the sphere and the flat surface the radius of curvature is very small, hence the surface energy is very high. This surface energy can be decreased by a decrease in surface area, which in turn creates a decrease in density of the material below the surface thus establishing the vacancy concentration gradient required for diffusion flow. In the surface diffusion flow the mechanism is also the same as that of volume diffusion, and a vacancy concentration gradient is also assumed to exist. In the evaporation-condensation process it is well known that the vapor pressure above a surface is related to both surface tension and curvature, the pressure increasing with increasing curvature, and the vapor pressure is greater above a convex surface than above a concave surface.

In studying the decrease in pore volume, Rhines et al. observed that all the pores in the compact did not decrease in size as sintering proceeds isothermally. Although the total number of pores decreased steadily, the average pore size increased, so that small pores must have been somewhat absorbed by larger ones. In this case the pores are supposed to be isolated from each other. It is probable that if the evaporation-condensation process is at all operative, it will change only the shape of the pores and not their volume, and the same argument holds for the surface diffusion process. So that two most important processes for changing the volume of pores are therefore volume diffusion flow and viscous or plastic flow.

The approximation theory which is a strong supporting argument for the diffusional flow theory of sintering outlined by Rhines et al. is that the evaporation of metal in a small pore creates vacancy concentration in the neighborhood of the pores. Since the vapor pressure is higher in small pores than in large ones, the vacancy concentration is also higher in small pores than in large ones.

The flow of vacancies along the gradient thus created builds up higher concentration near a large pore, and evaporation must continue from small pores in order to maintain the equilibrium pressure. His argument against the viscous flow mechanism is that it takes more energy to form a dislocation than to form a lattice vacancy. This approximation seems to be impossible because of the relatively large distances involved and the slowness of the diffusion process in the condensed phase. So the possibility of the system is to destroy or eliminate the vacancy in the internal sinks in the crystals. Herring was the first to suggest that grain boundaries are the effective sinks of vacancies, and Alexander and Baluffi have verified this suggestion experimentally. They sintered a spool of copper wires and observed that tabular pores shrank uniformly as long as they were connected by a network of grain boundaries. When by prolonged annealing, the shrinkage ceased, so that the powder compacts cannot be sintered to the full density by annealing alone. In order to eliminate this residual porosity, the compacts were often repressed and resintered. Repressing followed by reheating caused recrystallization, which restored the grain-boundary network connecting the pores.

This experiment dramatically emphasizes the important role that grain boundaries play in densification.

**Liquid phase sintering:** There are many systems in which a considerable difference in the melting of the components exists, in these cases, sintering may be carried out advantageously above the melting point of the lowest melting constituent. Therefore this process will depend on the equilibrium diagram of the system. The presence of a liquid phase will considerably increase the rate of diffusion that increases the rate of alloying too, and will effect the sintering process in all of its aspects, especially if the melting part is sufficient to form a continuous matrix. The stages of liquid phase sintering are given in the approximation order of their existence in some cases, but these stages may overlap to appreciable extent :

- a) melting and liquid flow involving a rearrangement of solid particles,
- b) rapid dissolution of the small solid constituent and reprecipitation on the larger ones, and
- c) coalescence of solid particles involving slow densification.

The liquid phase sintering may be divided into systems in which (1) the liquid phase is only of intermittent character, and (2) the liquid phase remains throughout the high-temperature sintering procedure. In the first instance the liquid phase can exist only temporarily at a certain temperature and then absorbed by the base metal, diffusing into a solid solution or compound forming a sintered alloy which behave like a homogeneous compact.

In this case the liquid phase must be kept small enough so that the compact is not deformed by collapsing or rounding the corners. While in the second system, the liquid is not absorbed by the remaining phase during the treatment, it will act as a binder or cement for the solid particles, however, it can be present only in a relative limited amounts for reason of preserving the shape of the compact. After sintering, this binder or cementing material will govern the strength, toughness, and other properties of the final product, and the attractive forces between particles of the matrix material play only a comparatively small role. The theoretical study has been centered on a model in which the liquid phase should be large enough so that appreciable densification will occur.

In the first stage, large scale bulk movement of particles within the liquid phase causing rearrangement of particles and densification. The greater the extent of wetting the greater will be the driving force for this stage of sintering, and densification will increase with the increasing amount of liquid phase by this process.

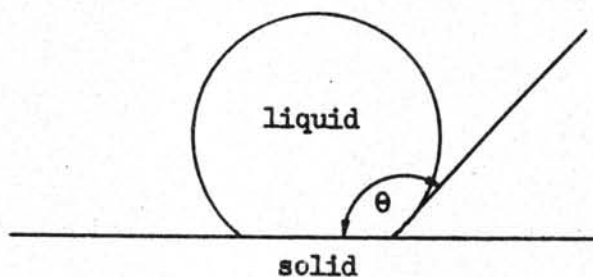


Fig. 1. The figure shows the contact angle between liquid and solid phases, when a liquid droplet is in contact with a solid surface .

By considering the contact angle ( $\theta$ ) of liquid droplet in contact with a solid surface as in Fig. 1., if the liquid phase completely wets the solid particles ( $\theta = 0^\circ$ ), they will remain separated by the film of liquid. In order to obtain result in liquid phase sintering successfully, the contact angle should be less than  $90^\circ$ . In case of non-wetting liquid phase, the contact angle will be larger than  $90^\circ$  and small droplets from the compact will occur during sintering. The extent of wetting can be improved by lowering the liquid-solid interface energy by diffusion or absorption method at the interface.

After the completion of the rearrangement stage, the second stage will take place involving solution and reprecipitation, i.e. dissolution of small grains and reprecipitation on the larger one take place. It is controlled fundamentally by the surface and interfacial tension of the phases. For these to occur, there must be at least a limited solubility of the solid in the liquid phase. During the process the liquid phase will dissolve the particle into the liquid by diffusion and the smaller particles will give the higher solubility compared with the larger ones. The solubility of the particle into the liquid phase will be limited due to the phase equilibrium diagram, and as long as the temperature is not increased this proportion does not change, even for an unlimited period of time. With increased temperature the amount of liquid cementing phase increases gradually in accordance with the ternary state of equilibrium. Upon cooling the element which dissolves in the liquid phase with the binder will reprecipitate on the undissolved particle surface because of

the decreasing solubility with falling temperature. A repeated sintering procedure would result in a diminishing of the finest particles and would thereby cause an increase in the size of the larger particles. This permits a change in particle shape which suggests a higher density thereby resulting in shrinkage.

The third stage of solid phase bonding stage will include coalescence and grain growth. In case of incomplete wetting of the solid by the liquid, there is no complete separation of the solid particles by the liquid but some contact between solid particles may occur. This condition results in the formation of solid skeleton (skeletal structure) within the compact which can seriously impede rapid densification by the first stage if it occurs early in the liquid phase sintering.

#### Neutron Activation Analysis (NAA)<sup>17-25</sup>

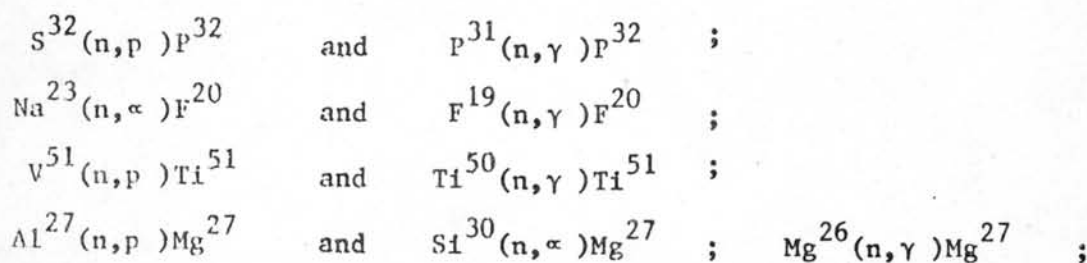
In Neutron Activation Analysis, samples are bombarded with neutrons from a reactor or other kinds of neutron sources and the elements are identified by the radioactive characteristics of the products of the nuclear reactions. Concentrations of the elements are determined by the intensity of radiation emitted. It is a very sensitive analytical method and avoids the need for corrections of reagents used in other methods of analysis. The major application is in tracer analysis, especially when only very small quantities of sample are available.



The Neutron Activation Analysis consists of two main steps :

1. Activation of the sample
2. Study of the induced radioactivity

In the first step, the sample will be activated to radionuclide by the  $(n,\gamma)$  reactions with thermal neutron which have the energy range about 0.025 eV or less while the  $(n,p)$ ,  $(n,\alpha)$ , and  $(n,n)$  reactions are produced by the fast neutrons having the energy range about 0.1 MeV to 14 MeV. In general practice reactors and isotopic neutron sources are the most available neutron sources using in the analytical purpose. The fast neutron activation analysis are not widely used as thermal neutron activation due to the cross-sections which are generally considerably lower on the same target nuclei and the combination of lower flux (except in the case that thermal neutrons are unavailable or lacking in sensitivity or specificity). In using thermal neutron activation in the thermal reactor, the fast-neutron flux in such out-of-core position may still be appreciable because of high values of error can be obtained for one element of interest, if the samples containing higher levels of the elements one or two units higher in atomic number(Z) can form the same radionuclide, via  $(n,p)$  and  $(n,\alpha)$  reactions, respectively, that the element of interest forms via the  $(n,\gamma)$  reaction, such as



$Ar^{38}(n,p)Cl^{38}$       and       $K^{41}(n,\alpha)Cl^{38}$       and       $Cl^{37}(n,\gamma)Cl^{38}$       ; and  
 $Fe^{56}(n,p)Mn^{56}$       and       $Co^{59}(n,\alpha)Mn^{56}$       and       $Mn^{55}(n,\gamma)Mn^{56}$

reactions, etc.. This error can be partially corrected by using the cadmium ratio which is the ratio of neutron flux without and with an appreciable layer of cadmium for that particular condition (irradiation position and the stable nuclide). Due to the fact that cadmium has high thermal neutron absorption cross-section ( about 2537 barns ) but comparatively low for epithermal neutrons, this error can not be perfectly corrected. The fast neutron activation is much preferred than the thermal neutron activation in the case of Nitrogen, Oxygen, Iron, Silicon, Phosphorus, Thallium, Lead and many other elements in the condition that the  $(n,\gamma)$  reaction produce low activity per unit weight due to low  $(n,\gamma)$  cross-section or low % abundance ( specific abundance ) or both, more sensitivity detection ( in case of Iron and Silicon ), emit gamma ray instead of pure beta ray (due to the  $(n,\gamma)$  reaction ) in the case of Phosphorus, Thallium, Lead, and produce a higher yield of gamma ray in some conditions.

In the second step or studying of the induced radioactivity, the characteristic radiations of the elements formed by the nuclear reactions in the activation will be detected by the detector equipped with the multichannel analyzer. From the resulted spectrum, the elements in the sample will be identified both qualitatively and quantitatively using the relation between the energy, decay time, the photopeak area and the calculation using Covell's method.

## X-ray Fluorescence Analysis<sup>26-31</sup>

The elements and the chemical compositions in a substance, mixture, compound, mineral, alloy, etc., can be determined by using X-ray fluorescence techniques. These techniques are based on the principle that when using X-rays from either X-ray tube sources or isotopic annular sources which gave exciting energy larger than the absorption energy of a certain element, that element will emit a series of discrete X-ray energies which possess its own characteristic. By studying this characteristic X-rays, the elements and their quantities in the unknown specimen can be determined.

The X-ray Fluorescence Analysis can be classified into two systems as: Energy Dispersive X-ray fluorescence (EDX) and Wavelength Dispersive X-ray fluorescence (WDX) systems, respectively. For EDX system, the primary X-ray source may be either X-ray tube sources or isotopic annular sources. The primary X-ray radiation will be collimated before exciting the specimen, and after exciting the specimen the fluorescent X-rays will be collimated again before being detected by the detector. The signal from the detector will be enlarged by an amplifier and selected for the required energy range by the Single-channel Analyzer (SCA) or Multichannel Analyzer (MCA) and recorded by the printer or plotter. For WDX system, the primary X-ray radiation (especially from the tube excited source) will excite the elements in the specimen, and the fluorescent X-rays will be collimated by a primary collimator before diffracting on the analysing crystal (according to Bragg's Law) which is rotated on a goniometer.

The diffracted X-ray will be collimated again before being detected by the detection system.

The equations concerning the Wavelength Dispersive X-ray fluorescence techniques are:

$$E = h\nu = \frac{hc}{\lambda}$$

and

$$n\lambda = 2d \sin\theta$$

where E is the energy  
 $\lambda$  is the wavelength  
 $\nu$  is the frequency  
c is the velocity of light  
h is the Plank's constant  
n is the order of reflection  
2d is the interplanar spacing

The first equation gives the relationship between energy and wavelength of the radiations, while the second equation, called Bragg's Law, gives the relation between the wavelength ( $\lambda$ ), the spacing of the diffracting crystal, and the angle ( $\theta$ ) through which the radiation is diffracted. By fixing the 2d value of the analysing crystal, and the order of reflection (n), the angle  $\theta$  ( or  $2\theta$  that usually obtained in the detection system ) will correspond to a certain wavelength. From the acquired data (net count in a unit time interval), the calibration curves will be plotted and used as a standard curve for a certain specimen set at a specific matrix condition.

Among the problems usually encounter in X-ray analysis, the matrix effects is the greatest problem, This matrix effects can be eliminated by using Standard Addition method, Dilution method, and Internal Standard method. Other methods are:

- double-channel absorption edge analysis,
- concentration increase and dilution method,
- fluorescence-absorption method,
- emission-transmission method,
- fluorescence-Compton scattering method,
- method of multicomponent analysis, and etc.

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These methods can eliminate the matrix effects in the powder form condition only. Other problems such as particle size effects, precision of the instrumental data, precision of the calibration standards, random errors, and human errors, etc., are considered to be only little effects which can be eliminated easily comparing with the matrix effects.

On comparison between EDX and WDX system, the advantages of each system can be concluded as follows:-

- for EDX system,
  1. EDX has higher speed over the single-channel wavelength dispersive system for quantitative analysis.
  2. EDX system with MCA has lower cost in comparing with multichannel WDX system.
  3. Measure all elements (expected and unexpected).

4. High ability in displaying data and ease in interpretation.
  5. Having fewer geometric constraints than WDX system.
  6. Using secondary fluorescer EDX system is easier in controlling spurious lines (from the anode assembly substrate and beryllium window sealing fluxes such as W, Fe, Cu, Ni, etc.) in the background than in the WDX system.
- for WDX system,
1. WDX is ten times more sensitive than EDX system, due to lower background counting rate.
  2. WDX has a detection limits lower than EDX and is suitable for very low atomic number element.
  3. WDX has one or two orders of magnitude of resolution (2-3 eV) due to the diffracting system, while, for the EDX system the best Si(Li) detector has resolution range about 150-160 eV .
  4. WDX can maintain the total X-ray flux greater than  $4 \times 10^4$  counts per second due to high resolution.
  5. Needless to use minicomputer coupled with the system for accurate quantitative analysis results.
  6. No serious dead time problem as in the EDX system.
  7. Needless to keep the Si(Li) detector at liquid nitrogen temperature.

Density Determination by Gamma Transmission Technique. 17,20,21,22.

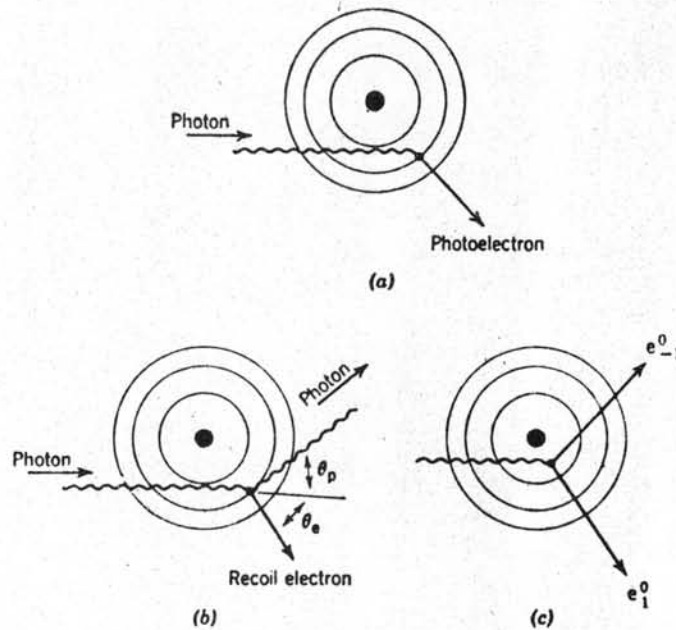


Fig. 2. Interaction of photons with atoms.

- a) Photoelectric effect,
- b) Compton effect,
- c) Pair production.

When gamma radiation interacts with material, the interactions occurred will depend upon the energy of the incident radiation, which can be classified as:

1. Photoelectric effect (see Fig. 2.a)

The photon of gamma radiation may impinge on an orbital electron of an atom and transfer all of its energy to the electron, resulting in the electron's leaving its orbit with a kinetic energy equal to the difference between the energy of the photon and the binding energy of

the electron. The ejected electron, called a photoelectron, may have sufficient energy to produce ionization of other atoms. The gamma ray is annihilated in the process. This effect occurs primarily at relatively low value of gamma energy.

## 2. Compton effect (see Fig. 2.b)

The photon of energy ( $E$ ) will collide with an electron as though the photon were a particle. The photon is deflected through an angle  $\theta_p$  and the electron (called a recoil electron) is deflected through an angle  $\theta_e$ . The effective mass of the photon may be calculated from the Einstein's equation,  $E = mc^2$ , and the principles of conservation of mass and conservation of momentum applied to predict accurately the direction of the photon and the electron after the collision. It is apparent that in this effect, also known as Compton scattering, the photon is not converted entirely to kinetic energy of the electron as in the case in the photoelectric effect. The Compton effect predominates at intermediate energy levels.

## 3. Pair production (see Fig. 2.c)

In this process, a high energy photon will, in the vicinity of a nucleus, be converted into an electron and a positron. Energy of the incident photon in excess of the equivalent of the mass of the electron and positron is converted into kinetic energy of the newly created pair. The energy equivalent of the mass of each particle of the pair is 0.51 MeV. Consequently, pair production cannot occur if the energy of the incident photon is less than 1.02 MeV. In this process energy is converted into mass.



The probability of pair production from a photon of given energy greater than 1.02 Mev is greater in heavy atoms than in light atoms.

If gamma radiation of intensity,  $I_0$ , is directed against a sheet of material of thickness  $x$ , the intensity of the emerging radiation,  $I$ , will be

$$I = I_0 e^{-\mu x}$$

where  $\mu$  is the linear absorption coefficient of the material.

This equation is valid for thin absorber with monoenergetic and collimated beam of gamma radiation. Using a standard specimen of a certain material knowing its density and thickness; when the thickness  $x$  is fixed, the attenuated intensity ( $I$ ) will correspond to its density, and the calibration curve between the attenuated intensity and the density will be constructed. By using this method the density of the unknown sample will be determined.

#### Detection System 17,22,26,27,28,29,30,32

The detection system used in these thesis experiments is composed of two major parts: the detector and pulse height analyzer.

1. Detectors, the detectors used in the experiments are:

- proportional counter

This kind of counter is usually filled with Argon, Xenon, or Krypton gas at a pressure somewhat less than atmospheric pressure. Most of the proportional counters are made with a side window, rather

than the end window, so that X-ray absorption can take place in a region of uniform electric field. When X-rays enter the detector, a small fraction pass right through, but the larger part is absorbed by the gas, and this absorption is accompanied by the ejection of photoelectrons and Compton recoil electrons from the atoms of the gas. The net result is ionization of the gas, producing electrons and positive gas ions which move under the influence of the electric field toward the anode and cathode, respectively. In moving under the influence of the electric field the multiple ionization or gas amplification will occur, resulting in  $10^3$  to  $10^5$  times of the initial single X-ray quantum. Each pulse which have pulse size proportional to the energy of the quantum will be absorbed at the electrode as a electric signal.

- scintillation counter

When radiations enter a Sodium iodide crystal activated with a small amount of Thallium, the Sodium iodide crystal emits violet light under radiations bombardment. (The absorbed radiations ionize some atoms, raise some electrons from the valence to the conduction band of NaI. These electrons then transfer some of their energies to the  $Tl^+$  ion. When the excited ion returns to its ground state, light is emitted.) The light-emitting crystal is cemented to the face of a photomultiplier tube, and shielded from external light by means of aluminium foil. A scintillation is produced in the crystal for every radiation quantum absorbed, and this light passes into the photomultiplier tube (PMT) and ejects a number of electrons from the photocathode made of Cs-Sb intermetallic compound.

These electrons will be multiplied in the PMT to about  $10^7$  times in less than a microsecond. This kind of detector can operate at the rate of  $10^5$  counts per second without losses.

- Semi-conductor or Solid-state counter (Ge(Li) and Si(Li))

This kind of detector produces pulses proportional to the absorbed radiation energy with better energy resolution than any other counters. For gamma rays, Germanium is used because it is heavier and is a better absorber than Silicon which is used for X-rays. Both contain a small amount of Lithium and must be operated at the temperature of liquid nitrogen ( 77 K or  $-196^\circ\text{C}$  ) all the time, in order to minimize (1) a constant leakage current through the detector, even in the absence of radiations, due to thermal excitation of electrons in the intrinsic region, and (2) thermal diffusion of Lithium, which would destroy the even distribution attained by drifting. These counters are suitable for intermediate wavelengths (energies) radiations because long wavelengths (low energies) are partially absorbed by the window and short wavelengths (high energies) are partially transmitted through the counter. Their counting rates varies up to 5,000 to 10,000 counts per second.

Comparison among these detectors, the semi-conductor detector has excellent resolution, while the proportional and scintillation counters have lower and lower resolution, respectively, as illustrated in Fig. 3.

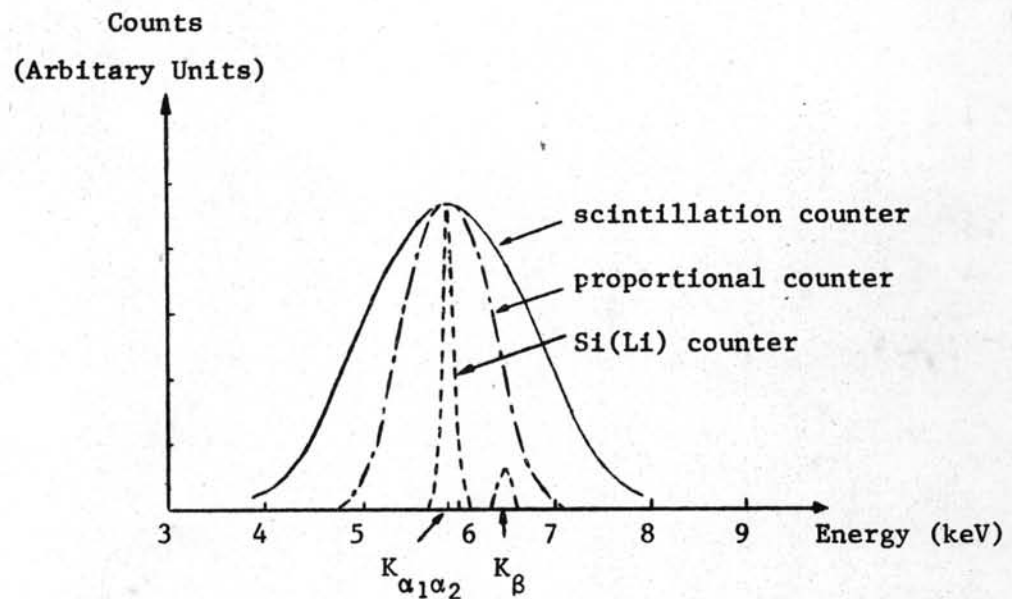


Fig. 3. Pulse-height distribution curves for three kinds of counters. The incident radiation is Mn  $K_{\alpha}$  ( $\lambda = 2.10$  Angstrom,  $E = 5.90$  keV) and Mn  $K_{\beta}$  ( $\lambda = 1.91$  Angstrom,  $E = 6.50$  keV). Among the three, the Si(Li) detector has the highest resolution, the proportional detector has lower resolution, and scintillation detector has lowest resolution.

2. Pulse-Height Analyzer, the pulse-height analyzer are the electrical circuits that can distinguish between pulses of different size and energy (wavelength) receiving from the detector. These circuits are:-

- a) Single-channel pulse-height analyzer (SCA)
- b) Multichannel pulse-height analyzer (MCA)

The SCA is composed of an anti-coincident circuit that rejects any pulse larger or smaller than the required voltage range of pulse heights by setting the lower level discriminator and the upper level discriminator, respectively.

This circuit works best when the required and rejected pulse heights have energies or wavelengths far apart. The MCA is composed of a many channels that are equivalent to the energy range required. It is designed to separate pulses from a detector (that receives incident radiation of many energies), by sorting pulses according to their sizes (amplitude), storage, and display. The MCA is actually a special-purpose computer with three functions:

1. Digitizing.

An analog-to-digital converter (ADC) converts the analog information contained in each pulse (amplitude in volts) into digital form, suitable for storing in a memory.

2. Sorting and Storage.

In the memory of the MCA, each channel will span an energy range due to the setting of conversion gain, and it will receive and store the information from the ADC unit.

3. Display.

The contents of the MCA memory (total counts in each channel) may be displayed visually as counts vs. channel number (radiation energies) on a TV screen or an plotter or recorded on printed tape or punched tape, or magnetic tape.

It may be concluded that in SCA the entire energy range is scanned serially in time by one moving channel, while in MCA, a large number of fixed channels covers the energy range and all channels simultaneously receive the count-rate information appropriate to each channel.