

Chapter: 2 Purification of Metals

2.1 Principle

In general metal purification and refining techniques depend upon the differences in physicochemical properties of a base metal and impurities. To get an ultra-high purity, a sequence of refining steps is required. These steps are fundamentally applicable in this order, chemical, electrochemical and physical methods. A substance is practically pure if its properties are determined by the atomic-crystalline structure. While the relative effect of impurities is negligible. Even low concentrations of impurities as one part in a million of the matrix metal can influence the physical properties as reported by Kopeczky [7].

2.2 Methods

For removing large quantities of different impurities, suitable methods of purification are hydrometallurgical and pyrometallurgical operations, aqueous precipitation techniques and fire refining, under appropriate conditions. However, further ion-selective methods can be applied in aqueous media to achieve ultra-high purity. The methods of purification of a metal can be classified according to the main property utilized in its separation. Usually a metal is extracted from a purified solution by the electrolysis or hydrogen reduction of a crystallized and dehydrated salt. Refining electrolysis or other different physical methods, including vacuum melting, distillation, zone melting, hydrogen-plasma melting and electrotransport can eliminate the traces of impurities. The results of an applied procedure may equally depend on the primary (gross) and the secondary (fine) purification steps.

2.3 Pyrometallurgical refining

Pyrometallurgy is a branch of extractive metallurgy and consists of the thermal treatment of minerals and metallurgical ores and concentrates to bring about physical and chemical transformations in the materials to enable recovery of valuable metals. Pyrometallurgical treatment may produce pure metals, or intermediate compounds or alloys, suitable as feed for further processing. Pyrometallurgical processes are generally

grouped into one or more of the following categories: drying, calcining, roasting, smelting, and refining. Most pyrometallurgical processes require energy input to sustain the temperature at which the process takes place. The energy is usually provided in the form of fossil fuel combustion, exothermic reaction of the material, or from electrical heat. When enough material is present in the feed to sustain the process temperature by exothermic reaction, the process is said to be autogenous [8].

2.4. Chemical metallurgical refining

A large number of chemical-metallurgical refining techniques can be applied due to differences in the chemical properties of a base metal and impurities. The principal chemical property is reactivity or affinity toward added agents such as oxygen, chlorine or sulfur. In the common fire refining process, when a reagent is added to a molten metal at an appropriate temperature then conditions are favorable if the Gibbs free energy change in the reaction for one mole of the reagent with the impurity element is more negative than that in the reaction with a base metal.

In the refining process an impurity is selectively reacted therefore its activity in the molten metal phase is continually decreasing. The resulting impure compound is taken up in the form of the slag or dross, which is practically not miscible with a molten metal. The activity of an impure compound in the produced phase is continuously increasing. It is especially advantageous if the compound formed from the removed impurity is volatile, and its activity is kept to a minimum by continuous removal (applying vacuum or flushing) of the produced gas. At high temperatures and in well-designed reactors, most systems may approach these equilibrium conditions in practical time intervals. Unless equilibrium is approached, kinetic conditions may dominate in determining the actual impurity concentration. [9].

2.5 Hydrometallurgical Purification

High purity metals can also be extracted from an aqueous solution by hydro- metallurgical methods. These methods remove a large number of impurities from a variety of base metals. Initial purification of a solution

by precipitation technique, is capable of removing large quantities of impurities. The remaining portion can be removed by fine purification techniques, usually by ion exchange or solvent extraction. A high purity base metal can be extracted from a solution by the following alternative three methods:

Method-1 Evaporation to dryness, followed by hydrogen reduction of a compound (usually a chloride of the metal).

Method-2 Precipitation of a metal (with NH_4OH as a metal hydroxide, or with Organic agents as oxalates, stearates or citrates) and calcination followed by hydrogen reduction of oxide.

Method-3 Cathodic reduction by direct electrolysis of a purified solution.

In order to avoid contamination, an applied procedure and reagents are selected with care for extracting a base metal from a purified solution. Generally metals are obtained from a solution phase in the powder form, requiring melting to produce bulk material in a compact shape [9].

2.6 Primary Purification

Using the cementation process, an impurity metal of more noble character than a base metal can be removed from the solution in metallic form. The contamination of a solution can be avoided by applying a base metal in high purity powder or granule form as a precipitation agent. This process may continue as long as the electrode potential of an impurity element is sufficiently high. The precipitated impurity metal covers the added metal particles. This porous layer does not prevent the progress of cementation. The kinetic conditions of the reaction are usually governed by the material transport (diffusion) through the boundary layer of a solution around the particle, and through a porous deposit. The former step controls the rate of the process. An efficient stirring of the solution, higher temperature and a large specific surface area of an added metal particle can increase the rate of the process. Hydrogen gas evolution and co-deposition can take

place especially at higher acid concentrations. Generally, it contributes to the loosening of a deposited metal layer on substrate. Some dissolved metals can be partially eliminated from the solution by hydrolytic precipitation in the hydroxide form at a suitable pH value. Initially metals are processed in an acidic medium solution, hydrolytic precipitation can be achieved by consuming much of the free acid. Acid liberated during hydrolysis requires further addition of a neutralizing agent, so that salt produced could not contaminate a solution. It is practically achieved by using an oxide or hydroxide of a base metal. The precipitates of an amphoteric metal, capable of forming dissolved hydroxo-complex anions, are re-dissolved on increasing the pH above the range of efficient precipitation. Examples are Cr (III), Al (III), Pb (II), Sn (II) and Zn (II). The removal of iron (III) by hydrolytic precipitation has an additional purifying effect. At the lower pH, the hydrolytic reaction produces a complex of $\text{Fe}(\text{OH})_3 \cdot x\text{H}_2\text{O}$, capable of adsorbing a significant amount of metal ions (As, Sb, Sn, Ge, Te, etc.). At high pH, Fe(III) hydroxide tends to form the $[\text{Fe}(\text{H}_2\text{O})_2(\text{OH})_4]$ type anionic complex species, which are especially efficient in adsorbing cations. The precipitated hydroxide forms a gel type material with a high specific surface and a high content of retained solution. Coagulation of a precipitate retains the adsorbed impurities by occlusion as reported by Horvath and Mihalak [9]. Impurity metals can be efficiently removed from a solution by adding anions that form insoluble compounds with a cation to be eliminated. The most frequently precipitated compounds are sulfides, sulfates and carbonates, but some metals can be precipitated as chlorides, oxychlorides, phosphates or oxalates. This method does not always require large changes in pH value of a solution, to allow selective precipitation. Pre-treatment of a solution using different precipitation techniques can remove significant amounts of impurities. To design separation procedures for the practically important cations, known solubility data and set chemical techniques can be used as the basis. Generally aqueous solution treatment is supplemented with additional steps of metal extraction. A pure metal is extracted from the purified solution either by hydrogen reduction of a crystallized salt or by direct electro winning.

However, for the preparation of ultra-high-purity metals, the steps of bulk purification need to be followed by further (fine) purification of a solution by ion exchange or solvent extraction as reported by Monhemius [10], Hartinger [11], Sillen [12], Hogfeldt [13], Sandulescu [14], Erdy [15], Habashi [16], Meyer [17] and Zwicker [18].

2.7 Secondary or Fine purification

The distribution between the aqueous solution and an organic phase is a best chemical property for separating dissolved metal ions. An organic material constituting the cation or anion exchange resins and liquid extractants, also contains counter-ions (cations or anions). They may be exchanged for the corresponding complexed ions of a metal in solution. The strength of sorption is practically characterized by the equilibrium distribution coefficient. It refers to the amounts of a metal ion in the unit volumes of the organic (solid or liquid) and the contacted aqueous solution phases, respectively. The preference of the organic phase for one of two competing metals can be expressed by the selectivity coefficient, which is a ratio of the respective distribution coefficients. The separation of metal ions in solution can be effected by applying selective sorption and/or elution. It is carried out by adjusting the chemistry of an aqueous solution in such a way that favors selective uptake or release of one metal by an organic phase. In cases when a larger number of different elements have to be separated. The column operations can be considered as a large number of repeated batch equilibration steps. The separated pure metal is obtained in a certain volume fraction of the effluent. The separating effect of ion exchange can be enhanced and supplemented by applying such aqueous media where a metal ion can be complexed, and forming anionic species. The stability of complexes may show great differences and may depend on the concentration of the complexing anions in the solution. The negatively charged complexes are subject to sorption of different strengths on anion exchange resins and are released from cation exchange resins. Anion exchange can sharply differentiate between transition metals, so, ultra-high purification can be carried out initially by this technique.

Chloro-complexes of a large number of metals can be formed at suitable concentrations of chloride ions in the solution. To achieve the ultra-high-purity, it is best to avoid the introduction of foreign cations, so the complexing chloride ions are supplied in the form of pure hydrochloric acid. Sorption functions may be determined directly by elution tests, using ion-exchange columns as reported by and Kraus [19]. In cases where precipitation, unstable oxidation states or high values of the distribution coefficient cause practical difficulties, batch equilibration is required for the examination of ion exchange characteristics Kekesi in 1994 [20]. Those impurities not forming anionic complex species can be directly separated by anion exchange if a base metal is strongly complexed and sorbed under the applied conditions. The differences in sorption characteristics of the elements in hydrochloric media propose that an optimum elution process, different concentrations of HCl for rinsing, can be compiled for an overall purification of the majority of base metals as reported by Kekesi in 1995 [21]. A proper adjustment of the HCl concentration in the eluent fractions requires elution experiments with bench-scale columns as reported by Kekesi 1997 [22]. Cation exchange may be used in addition to anion exchange steps for the separation of cationic impurities from a base metal which can form only neutral complex species, even at higher HCl concentrations. The method of solvent extraction is also based on the distribution of metals between the aqueous and the organic phases similar to ion exchange. The reactions involved are similar to those applied in ion exchange, but the equilibration and the subsequent separation of the two phases imply more complicated technology. A further disadvantage is the lack of chromatographic (dynamic) operation. Therefore, solvent extraction is usually applied for special purposes. Highly selective (chelating) reagents have been developed for the extraction of some metals. Separation by solvent extraction can initially find application in removing specific impurities, for which common purification methods are less efficient as reported by Dimitrov and Bigot [23].

2.8 Electrochemical Purification

Electrowinning may contribute to the purpose of purification besides extracting the metal from the electrolyte solution. Electrowinning requires insoluble, inert anodes, usually made of a noble or passivated metal, but pure graphite may also be used. If the starting cathode is made of the same metal as the one to be extracted from a solution then further processing requires no separation of the cathode layers. Other conditions for convenient mechanical separation of the produced deposit from the substrate have also been found. Cathodic deposition may offer a significant purifying effect due to the different electrode potentials of metals in an electrolyte solution. The characteristic electrode potential of a reduction process, is composed of the equilibrium electrode potential and the over potential. A higher (more positive) equilibrium electrode potential means a stronger tendency of cathodic reduction for a metal. The relative values of the electrode potentials determine the order of cathodic deposition of competing cations. In order to obtain selective cathodic deposition of a metal, it is necessary to ensure that its electrode potential will be sufficiently higher than that of the other metal ions in the solution. A net current density of a cathode depends on a continuous supply of ions carried by diffusion. It requires a lower effective concentration of the discharged ions at the cathode interface than in the bulk solution resulting in a shift of the electrode potential, defined as the diffusion over potential as reported by Erdey Gruz [24] and Kekesi [25].

High-purity cathodes may generally be obtained by electrowinning, on the condition that a potential is regulated by limiting a practical range of the current density. In order to extract a high purity metal, it is usual to deposit the more noble impurity metals at a higher initial cathode potential. The lower this initial potential is set, the more of these impurities will be eliminated, but more of the main metal will also be lost by codeposition. After replacing the cathode with a high-purity starting sheet, a base metal is deposited at a suitable cathode potential, which leaves the less noble impurities in the electrolyte solution. Most metals can be electrodeposited from aqueous solutions on solid electrodes under

proper conditions. The limitation is imposed by the possibility of hydrogen evolution. In order to deposit a metal from an aqueous medium, suppressing the desired cathodic process, the effective electrode potential of a metal has to be higher than that of hydrogen. The absolute value of the hydrogen over potential is usually increased by applying smoother cathode surfaces. Sufficiently negative potentials of hydrogen evolution with a given metal as cathode material can be attained by increasing the pH and by setting a lower temperature and higher current densities for electrolysis. In this way, metals with low standard electrode potentials, such as zinc or manganese, can be electrowon from neutral (slightly acidic) electrolytes of sufficiently high metal concentration. If all efforts fail to ensure an acceptable current efficiency (as in the cases of the most reactive metals, such as Al, Mg and Ti), then electrowinning can be carried out from a molten salt electrolyte. Metals produced by electrowinning may be further purified by placing them in electrorefining cells as anodes. The metal is anodically dissolved in the electrolyte, and is deposited at a cathode as highly pure material. Noble impurities, of significantly higher electrode potential, tend to remain undissolved and mixed with the fallen particles of an anode, making a slime by-product. Reactive elements of lower electrode potential may enter the electrolyte but they do not endanger cathode purity until their concentration and electrode potential increases to a critical level. If a base metal in the solution has a relatively low electrode potential, it is advisable to separate the anode and cathode compartments in the cell with a porous diaphragm or even by an ion-exchange membrane. In the case of electrowinning with insoluble anodes, this separation also prevents the direct transport of the hydrogen ions produced at an anode across a cell to a cathode. In the case of electrorefining, separation of an anode and a cathode compartment allows the circulation of the anolyte out of the cell for purification before it is fed to the cathode compartment. When it is warranted by extreme purity requirements, the electrorefining step may be repeated. For this purpose, those types of electrolytes (e.g. chlorides, nitrates) are preferred whose basic components causing trace occlusions

in the cathode are efficiently removed by the following melting step, carried out under vacuum or in a proper gas atmosphere. [26]

2.9 Solid-Liquid Equilibria

The solubility of impurities is different from each other in the molten and the solid metal phases. The portion of impurities rejected by the solidifying a base metal is pushed along by a solidification front. If the direction and rate of solidification is controlled by proper temperature gradients, these kinds of impurities can be concentrated in a moving molten zone which carries them to one end of a metal rod. Higher soluble impurities in the solid phase are partially rejected by the molten zone and so they are concentrated. The equilibrium partition (or segregation) coefficient is the ratio of the equilibrium concentrations of the impurity in the solid and in the liquid phases. The efficiency of a purification method can be enhanced by applying relatively longer specimens, slower rates of zone travel and narrowing the molten zones, in which case the technique is considered as zone refining. When the impurity content of the liquid phase is continuously increasing during the operation, then a single pass of the molten zone cannot yield any appreciable degree of purification. High purity can only be achieved by applying sufficiently pre-refined material and multiple (15-25) passes of the zone. Impurities with effective partition coefficients less than unity move in the direction of zoning, and are concentrated at the end of the rod, while those with partition coefficients higher than unity behave in the opposite manner. However, no segregation can be expected when the value of the partition coefficient does not differ significantly from unity. The purifying effect of zone melting is most often combined with that of melting in vacuum or reactive gas. For volatile metals, an inert or reactive gas atmosphere is required. The metals purified by zone refining are Fe, Mg, Al, Cu, Mo, W, Co, Re, Ti, Zr, Pb, Zn, U, Sn, Bi, Sb, In, Be, Ga, Pt and Si as reported by Meszaros [27].

The purity of the product is highly sensitive to the material of a container as a source of contaminants. The use of a container is avoided by the floating zone melting of vertically arranged specimens. The

molten zone is stabilized by the surface tension of the material and the electromagnetic forces of the induction coil. This technique has the added advantage of efficiently stirring the molten zone, which enhances the transport of impurities and results in higher effective segregation coefficients. Zone refining is a slow and expensive technique. Therefore, it is usually applied as the final purification step in the preparation of ultra-high-purity metals, following large-scale purification by less expensive and more generally efficient methods. Fractional crystallization is a purifying method based on the segregation phenomenon, just as zone refining. However, fractional crystallization is capable of removing higher amounts of impurities and offers significantly higher levels of productivity. This method is practically combined with continuous casting. During solidification, impurities with low partition coefficients are left behind in the molten phase. In order to reduce the thickness of the diffusion layer at the solidification front, the liquid pool of metal is intensively stirred. Continuous production of high-purity crystals is facilitated by a constant bleed of the molten metal, collecting the segregated impurities, from the top of the mould. The achieved purity depends on the rate of solidification and the speed of casting [27].

2.10 Selective Volatilization

2.10.1 Distillation A base metal can be separated from impurity if there is sufficient difference in their vapor pressure. This technique applies to relatively volatile metals, having high vapor pressures at suitable temperature. Although distillation requires a relatively sophisticated operation, it offers higher efficiencies.

The vapor pressure of a substance is an exponential function of temperature. The numerical forms of these functions are readily available in compilations of thermochemical data. The vapor pressure of the impurity also depends on its activity in the condensed phase as illustrated by Kubaschewski [28] and Stull [29].

Evaporation is an endothermic process generally requires heating and is mostly restricted to the surface in contact with the gas atmosphere. It is

because high metallostatic pressures, surface tension and heat of evaporation tend to prevent bubble formation in liquid metal baths. Therefore, the specific surface area of the liquid should be increased to a technical maximum. Due to the mechanism of surface evaporation, the concentration of a volatile component decreases at a thin boundary layer. This effect creates the driving force of diffusion. Distillation of metals consists of four consecutive process steps (i) Transport of volatile components to the surface of the metal (ii) Evaporation (iii) Transport in the gas phase (iv) Condensation. The rate determining step is generally evaporation at low pressures and moderate temperatures, whereas diffusion through the boundary layer in the melt is expected to be dominant at a higher temperature. The transport process through the boundary layer in the gas phase can influence the rate of distillation only at high vapor pressures as reported by Winkler [30]. Even in these cases, the removal rates of some metallic impurities (e.g. Fe, Cu, Ca, S) are not satisfactory, and therefore the process is not perfectly suitable for overall purification. Depending on the raw material, metal grades of greater than 99.95% are commonly achieved. A similar procedure is the reaction of the raw metal with the higher oxidation state halide vapor of the same metal at an appropriate temperature. Due to the change in the total volume of the gas, lower pressures shift ^{ed} equilibrium of the reaction to the right. The subhalide vapor of metal halide leaves the reactor to be purified in a rectification column, and it finally enters the second reaction chamber to undergo disproportionation at a reduced temperature and increased pressure. The method has reached the semi-industrial level for aluminum and titanium purification with chloride compounds [31].

2.10.2 Electrotransport

The charged particles may migrate in a solid piece of metal under the effects of an electric field. This phenomenon is applicable to the purification of metals if the velocity of migrating impurities is different or opposite in comparison with that of a base metal. The longitudinal particle flux in a relatively long bar of a metal placed along the imaginary x-axis is generally a result of complex driving forces caused by the

gradients of concentration, temperature and electric potential. A sufficient duration of electrotransport brings about concentration gradients resulting in equal magnitudes of diffusion fluxes in opposite directions. In practice it enables only very thin wires to be purified by this method. Due to the slow rate of migration, the operational cost is extraordinarily high. So the application of electrotransport to a metal purification is warranted only in special cases of extremely valuable materials and ultra-high levels of purity. Electrotransport is mainly efficient in removing traces of oxygen, nitrogen, carbon or hydrogen, since the mobility of interstitial impurities is significantly higher than that of substitutional elements. This property makes this method a good complement to zone refining, which is efficient for dissolved impurities.

Note: A general schematic procedure of a metal purification has been shown in the Figure 1.

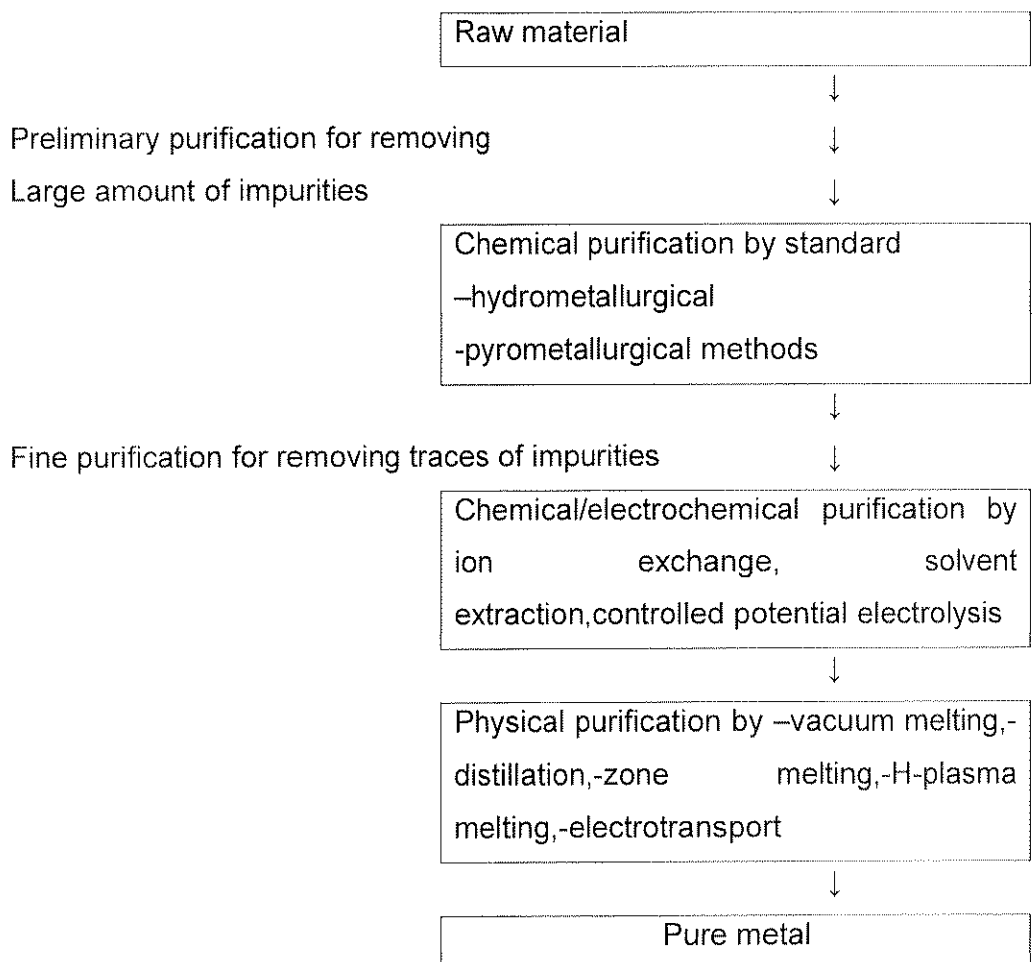


Figure1. A general schematic procedure of a metal purification

2.11 Purity Evaluation

Suitable analytical results are required for the development of purification processes, assessment of purity and characterization of the product. In most cases, the typical range of ultra-high purity is 6-7 N, having a total impurity concentration of the order of 0.1-1.0 parts per million (ppm) in mass so the sensitivity of the analytical method must be very high (usually of the order of 0.001-0.01 ppm).

2.11.1 Direct Indication of Purity

In order to know the the purity of the base metal matrix a systematic analysis of the possible number of impurities is required. The best and convenient methods of analyzing metallic impurity elements are atomic absorption spectrometry (AAS) and inductively coupled plasma atomic emission spectrometry (ICP AES) or ICP mass spectrometry. Usually the precision of the method increases by matrix matching in the standard and blank samples, or by preliminary separation of the major components and pre-concentration of the impurities. The most advantageous direct method of providing a complete analysis of high-purity metals is spark solid source or glow discharge mass spectrometry (GDMS). In this method the sensitivity is very high, and contamination is excluded by generating the ions directly on the prepared solid metal samples. For the analysis of nonmetallic light element impurities (C, N, O and H) in the gaseous form conventional technique of gas chromatography, using infrared or thermal conductivity detectors can be applied. Oxygen, nitrogen and hydrogen are determined after vacuum or inert gas fusion of a metal, while carbon and sulfur are typically determined using a high-temperature combustion method. γ -rays Spectrometry is a sensitive analytic method applied to direct purity evaluation of the non metallic elements as given by Issihiki and Fukuda [32]. Neutrons can be particularly important, which are readily available in nuclear reactors, and are used for activation purposes but for the analysis of light elements (C, N, O), photon irradiation, which implies the (γ, n) type reaction. In order to suppress unwanted radionuclides and complex nuclear reactions, the energy of irradiation is of essential importance as reported by Engelmann [33]. In some cases, the (γ, n) reaction cannot be

suitable, such as for analyzing oxygen, because the produced ^{15}O radioisotope has a short half-life (2.03 min), and some coexisting metallic impurities may be activated to a disturbing level as reported by Engelmann [34]. For the radio-activation analysis of oxygen, especially in reactive media, irradiation by charged particles [34, 35] can be the only way to achieve high precision and sensitivity as reported by Issihiki et al [35].

In the cases of iron, chromium, nickel and aluminum as the base metal, neutron activation analysis plays an important role in determining the residual impurities that remain after purification as reported by Issihiki and Igaki [36], Issihiki et al [37], Igaki et al [38], and Issihiki et al [39]. In the case of cobalt, neutron bombardment would induce strong activity from the matrix (^{59}Co) through an (n,γ) reaction. Therefore proton activation analysis (PAA) at an energy level lower than 11MeV is more suitable for the analysis of trace impurities in ultra-pure cobalt specimens. The most sensitive method for analyzing light element is the charged particle activation analysis (CPAA). The effect arising from the activated surface oxide layer can be easily eliminated by subsequent etching. In order to reduce the level of the background activity, and to enhance the sensitivity and accuracy, it is necessary to separate radionuclides. The limit of accurate oxygen detection in an iron matrix can be in the parts per billion (ppb) range after applying proper chemical separation. While on the other hand, radionuclides with different half-lives can be precisely distinguished and detected by repeating the γ -ray spectrometry several times during the cooling period. This method is capable of multi-element analysis of purified samples below the parts per million levels as reported by Issihiki et al in 1984 [40]. Modern instrumental methods are favourable for the chemical analysis of ultra-high-purity metal samples due to their sensitivity, accuracy and scope requirements. The precise and accurate impurity analysis on a trace level requires sophisticated, expensive and time-consuming procedures. Determination of the overall purity level depends on the accuracy, precision and completeness of an analysis, which has to cover all the appreciable components in a metal matrix [40].

2.11.2 Indirect Indication of Purity

There are many properties that are sensitive to the presence of trace amounts of foreign elements in a base metal matrix. Mechanical properties, such as yield stress, less or re-crystallization temperature after a standard cold work are straightforward to determine and are helpful in comparing a series of samples. The most practical indication of purity is electrical resistivity, measured under specified conditions. The resistivity of a bulk metal can be expressed as the sum of three principal contributions as reported by Kittel [41] and Weisberg [42].

Usually the residual resistivity ratio, as a measure of purity, is expressed as the ratio of the resistivity at room temperature to that obtained at a temperature close to kelvin zero. A sufficiently low temperature has to be reached in order to examine high-purity materials. In earlier practice, the more available liquid hydrogen was used to set the low temperature point (20.4 K), but currently the temperature provided by liquid helium (4.2 K) has become generally accepted to express the residual resistivity ratio (RRR) as reported by Kurasaka et al [43].

A magnetoresistivity term was be used for magnetic metals, due to the spontaneous magnetic field in the material. However, it can be eliminated by superimposing an external (longitudinal) magnetic field. A further resistivity contribution may arise from the scattering of electrons by the surface of the metal. The electrical resistivity of different iron specimens under an applied longitudinal magnetic field depends upon the temperature. The specimens of 352 RRR and 10410 RRR values correspond to purity levels of 3N and 6N, respectively show the calculated phonon scattering term, if the mean free path of an electron is commensurated with the diameter of a specimen as reported by Mende [44] and J.Peterseim [45].

The level of purity was expressed by the changes in the residual resistivity only if all the impurity content is homogeneously dissolved in a base metal matrix. The effects of segregation or precipitation may lead to the false assessment of chemical purity. Therefore, the use of residual electric resistivity for such purposes requires appropriate preparation

and measurement techniques, assuring the proper state of the impurities and excluding any further reactions, especially internal oxidation.

2.12 Comparison of Achieved Purity Levels

It is not always easy the purity comparison of different materials. All the impurities can not be analyzed due to incomplete direct analytical results. Therefore, the term nominal purity is frequently used for commercial purposes, meaning that some selected impurities are analyzed, but others are not. Usually this shortcoming is aggravated by the precision and detection limit factors, which depend strongly on the method and the operator. The application of measured RRR values for the comparison of purity also implies some difficulty. The normalization of a treatment preceding RRR testing is important if this indirect indication is to be used as a measure of material purity. If the examined metal is of ultra-high purity, as indicated by measured RRR values of the 10^4 order of magnitude, and the diameter of the wire specimen is comparable to the mean free path of the electrons then size effect has to be taken into consideration. If the size effect is appreciable, the usual practice is to convert the directly measured RRR values into ones representing the bulk material, excluding the resistivity contribution due to the scattering of electrons at the surface as reported by Mimura and Ishikawa [46]. Exact impurity assessment is directly possible in the case of samples obtained by the same purification procedure, exhibiting the same or similar relative impurity concentrations if impurities may have very different coefficients of influence on electrical resistivity. In other cases, the use of low temperature resistivity also requires the analytical data of the major components. The purity levels achieved in different laboratories and for different metals may be compared by RRR results. Reported values by Ishikawa-Issihiki [47] and the corresponding processes of purity evaluation by the RRR results is uncertain in some cases, due to unspecified or improper sample preparation.