

CHAPTER 2

LITERATURE REVIEWS

2.1 Glass-ceramic materials

2.1.1. Formation of glass-ceramics

In glass manufacture the formation of crystals or crystallization or devitrification is undesirable as it can change basic properties of glass such as viscosity and coefficient of thermal expansion, which leads to many problems. On the other hand, crystallization is required to form glass-ceramic materials. Glass-ceramic was accidentally discovered by S.D Stookey at Corning Glass Works, USA [6, 7, 8]. Glass-ceramics can be formed by the control of nucleation and subsequent crystallization of appropriate parent glass composition. The nucleation and growth of crystals based on a simple thermal treatment process are shown in Fig.2.1, starting from the formation of nuclei (a) then the growth of crystal on nuclei (b) and finally the formation of glass-ceramic microstructure (c). The process steps of producing glass-ceramics are shown in Fig.2.2 with respect to temperature and time.

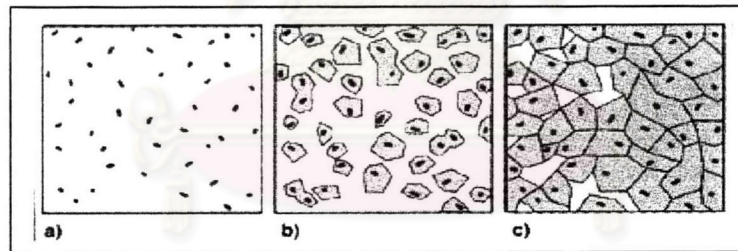


Fig.2.1 The formation of glass to glass-ceramic [7]

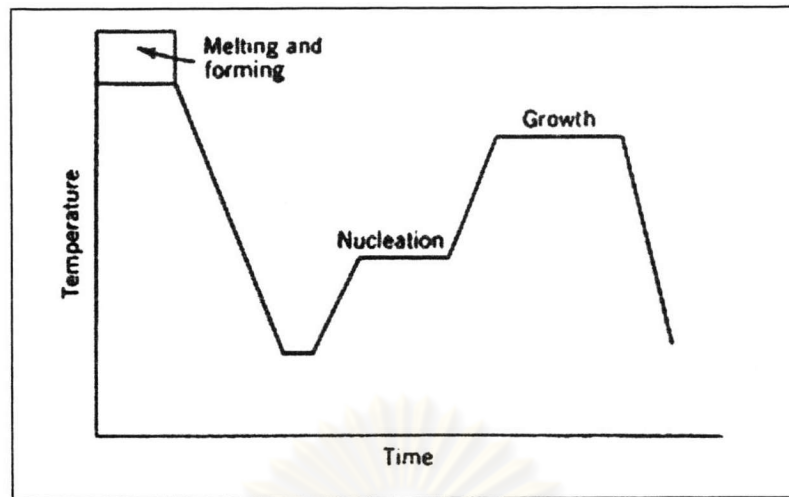


Fig.2.2 Heat treatment process for producing glass-ceramics [9]

The material is melted and formed at high temperature then cooled down to room temperature. At this stage the material may contain some phase separation, some very small nuclei or crystals or may be completely homogeneous. The material is then re-heated slowly to avoid the occurrence of thermal shock up to an appropriate temperature for nucleation. The material is held at this nucleation temperature for a period of ~1 to 2 hours. Once the nucleation is completed, the material is further heated to an appropriate temperature for the growth of crystalline phases. This crystallization temperature is chosen to minimize the kinetics of crystal growth rate in order to obtain the desirable phases and avoid deformation of samples, unwanted transformations within the crystalline phases, or re-dissolution of some of the phases. The nucleation and crystallization temperature can be varied depending on the heat treatment process and composition of the parent glass with nucleating agent as well as on the phases and properties desired in final body [7, 9].

Another method of making glass-ceramics has been developed recently. This method involves the sintering and crystallization of powder glass. The development of glass-ceramics via this method has many advantages superior to those of bulk-crystallized glass-ceramics. The traditional ceramic fabrication processes such as slip casting, pressing and extruding can be used in this method. Glass-ceramic coating on

metals can be applied by using this process. The greatest advantage is the ability to use surface imperfections in quenched frit as nucleation sites. The process making glass-ceramic from glass powder is shown in Fig.2.3. A quenched glass is ground into fine powder then sintered. The powdered glass compact (a) is transformed to a dense sintered glass with some surface nucleation sites (b) and finally formed glass-ceramic materials (c).

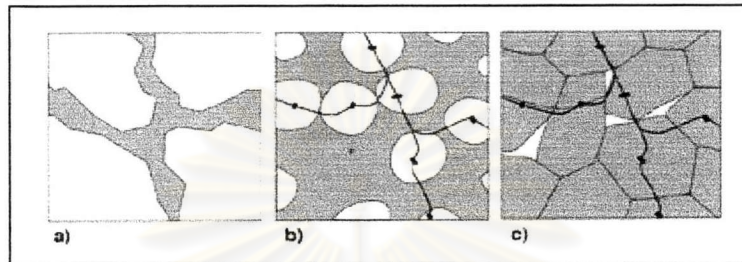


Fig.2.3 Formation of glass-ceramics from glass powder [7]

2.1.2. Properties of glass-ceramics

Glass-ceramics contain many different kinds of crystals in the glassy matrix causing some of their properties to be superior to those of glasses, ceramics and metals. Glass-ceramics are generally stronger than traditional ceramics by the fact of a wide crystal distribution and considerably less porosity. Thermal expansion of glass-ceramics is very low (near-zero) when compared with the parent glass, which allows it to be very highly resistant to thermal shock [10]. Glass-ceramics also show high chemical durability, which can be controlled by the nature of crystals, the glass phase or the nature of the interface between the crystal and glass-phase. These properties mostly depend on the crystalline phases and glassy phases. Therefore these properties can be controlled by either developing the nucleation and crystallization heat treatment process or varying the parent glass compositions [9, 8, 11].

2.2 Kinetic theory of nucleation and crystallization

Crystals usually form in glass by nucleation and growth mechanisms. In order to form crystals, the nucleus must overcome two energy barriers, which are the kinetic

barrier and the thermodynamic barrier. Nucleation rate (I), crystal growth rate (u) and the volume fraction of crystallization are three main factors normally used to determine whether or not the system will form a glass [10]. Nucleation rate (I) and crystal growth rate (u) are plotted together with correspondence to temperature (T) as shown in Fig.2.4. Initially the formation of nucleus (nucleation) with a critical size (radius, r^*) is required to introduce the subsequent growth of crystal.

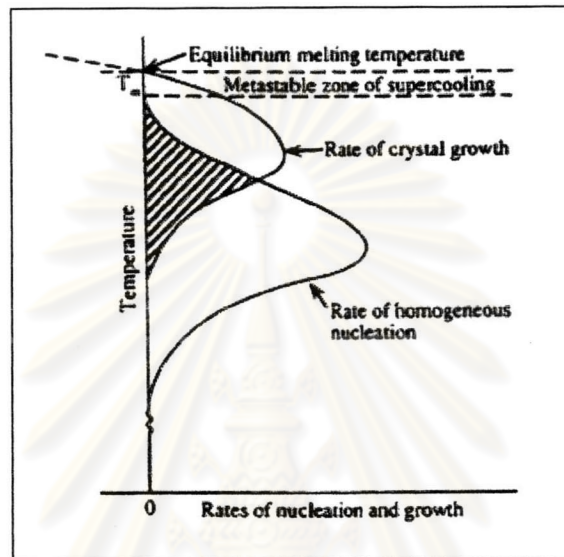


Fig.2.4 Nucleation and crystal growth with respect to temperature [10]

It is noted that the overlap between two curves represents the ability of the liquid to form glass during cooling with the temperature lower than T_m . The smaller size of the overlap leads to easier formation of glass without crystallization [10]. This confirms the fact that crystallization would never be formed without the presence of nucleus.

The nucleus can be formed as two different types, depending on the appearance of foreign boundaries such as substrate, grain boundaries, catalyst, etc. If the foreign boundaries are present in the system, a heterogeneous nucleus tends to be formed. On the other hand, if there are no foreign boundaries in the system, a homogeneous nucleus tends to be formed. The heterogeneous nucleus is the most common type of nucleus formed in glass-ceramics [6, 7].

The thermodynamic process of nucleation must be accompanied with the decrease in total free energy (ΔG). The total free energy consists of two main factors, which are a volume contribution and a surface contribution as described in eq. 2.2.

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \gamma \quad (\text{eq. 2.1})$$

The first term ($-\frac{4}{3}\pi r^3 \Delta G_v$) is the change in volume free energy per unit volume resulting from the formation of nuclei. The second term ($4\pi r^2 \gamma$) is the change in surface free energy per second resulting from the enlargement of the nucleus against the opposing surface tension (γ) of the environment. At any temperature below T_m the atoms in liquid are able to form a stable nucleus when ΔG is negative. Therefore the surface free energy term must be smaller than the change in volume free energy [6, 7, 10]. Fig.2.5 shows free energy of crystalline nucleus as a function of its radius at the temperature lower than T_m .

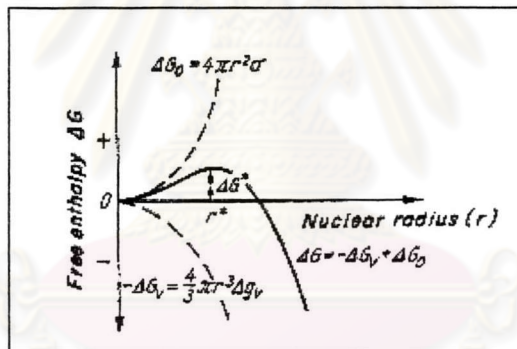


Fig.2.5 Free energy (ΔG) as a function of nucleus size (r) [6]

Consider the system without foreign boundaries or homogeneous nucleation. When a spherical embryo (a group of atoms) of radius r is very small, the surface energy term is high and dominates and then the total energy is increased. The embryo in this situation is unstable. Once the embryo has grown to a critical size with radius r^* it is then stable and called a nucleus. The radius r^* of the critical-size nucleus is determined and given by

$$r^* = \frac{-2\gamma}{\Delta G} \quad (\text{eq. 2.2})$$

Upon further growth of the critical-size nucleus, the total energy is decreased and volume energy term becomes dominant instead of the surface energy term. The nucleus in this situation is stable and ready to be a precursor of crystal growth.

When foreign boundaries such as a solid surface or substrate are involved in the system or there is heterogeneous nucleation as shown in Fig.2.6, atoms in the supercooled liquid attempt to form a nucleus (called a "crystal cluster") in contact with the substrate at the angle of θ .

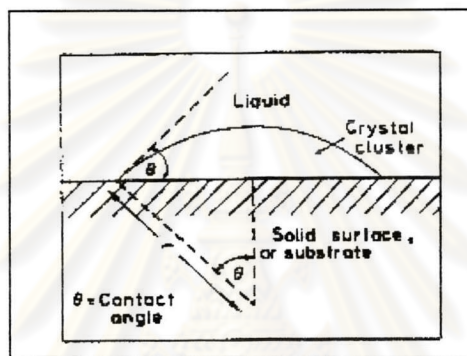


Fig.2.6 Heterogeneous nucleation on a solid substrate [10]

As well as homogeneous nucleation, the nucleus is formed when its radius equals a critical size (r^*), which is stable in the system [10]. The critical radius in this system has been determined and given by

$$r^* = \frac{-2\gamma_{LX}}{\Delta G_v} \quad (\text{eq. 2.3})$$

where, γ_{LX} is the surface energy of the liquid-crystal interface and ΔG_v is the change in free energy per unit volume. Consequently the total free energy of heterogeneous nucleation (ΔG^*_{hetero}) is similar to that of homogeneous nucleation (ΔG^*_{homo}), only the addition of contact angle (θ) is concerned, which is described as

$$\Delta G^*_{hetero} = \Delta G^*_{homo} \left[\frac{(1 - \cos \theta)^2 (2 + \cos \theta)}{4} \right] \quad (\text{eq. 2.4})$$

$$\begin{aligned} \text{When } \theta = 0 \quad \Delta G^*_{hetero} &= 0 \\ \theta = 90^\circ \quad \Delta G^*_{hetero} &= \frac{\Delta G^*_{homo}}{2} \\ \theta = 180^\circ \quad \Delta G^*_{hetero} &= \Delta G^*_{homo} \end{aligned}$$

It is noted that for the fully wetting substrate ($\theta = 0$), any size of embryo can grow without a thermodynamic barrier to nucleation. In the case of fully non-wetting substrate or spherical embryo, the total free energy of heterogeneous nucleation is equal to that of homogeneous nucleation.

In general the nucleation rate (I) of a nucleus with critical radius r^* can be described as

$$I = A \exp\left[-\frac{(\Delta G_E + \Delta G_D)}{kT}\right] \quad (\text{eq. 2.5})$$

Where, ΔG_E is the thermodynamic free energy barrier, ΔG_D is the kinetic free energy barrier, k is the Boltzmann constant and T is the absolute temperature (K).

The volume fraction (X) of crystallized material as a function of heat treatment time (t) is described as

$$X = \frac{V_x}{V_0} \cong \left(\frac{\pi u^3 t^4}{3}\right) \quad (\text{eq. 2.6})$$

Where, V_x is the volume of crystal and V_0 is the entire volume.

2.3 Time-temperature-transformation (T-T-T) diagram

As described previously the rate of nucleation and crystallization are a function of temperature. Thus the volume fraction of crystals at a given temperature can be calculated as a function of time by using eq. 2.7. The crystallization as a function of both time and temperature can be plotted consequently, which is called time-temperature-transformation (T-T-T) diagram as shown in Fig.2.7 This diagram is usually used for determining the presence of crystals in glass matrix [9,10, 11].

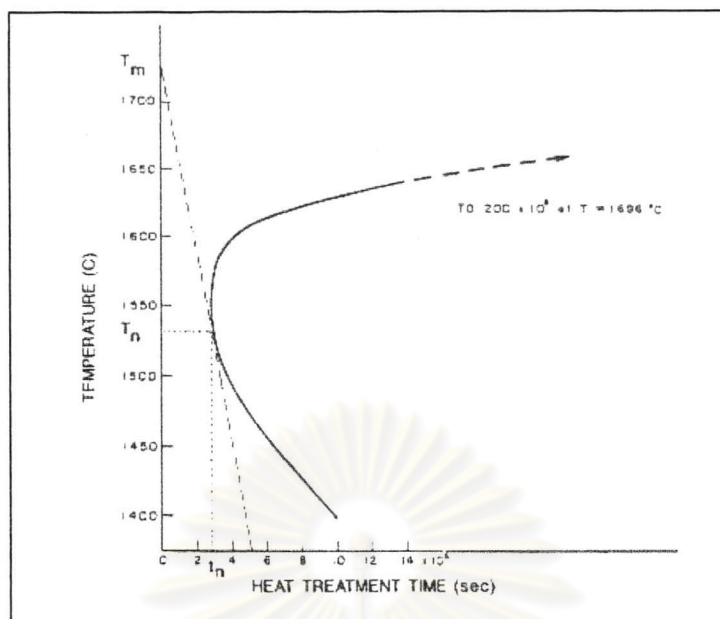


Fig.2.7 Time-temperature-transformation diagram [10]

Consider a liquid at a temperature near T_m . The time required for nucleation and growth is infinite because of inadequate thermodynamic driving force in the system. When the temperature is low enough to increase the driving force of nucleation and growth, the formed crystals can be detected at the particular time. The shortest time needed for crystallization is located at the nose of T-T-T curve at t_n , with respect to the temperature of the fastest crystallization at T_n which is maximum at the temperature T_n and time t_n . When the temperature is below T_n , the atomic mobility is decreased with the increase in viscosity that limits the rate of nucleation and growth and the time required for nucleation and growth is then become large again. Therefore the crystallization could not occur as long as the cooling rate is faster than the rate given by the tangent at the nose of T-T-T diagram [10, 11].

2.4 Zinc refinery process

The compositions of zinc waste generated from different plants can be varied depending on type of zinc minerals and materials adding during the zinc recovery process [2, 3]. Therefore, it is necessary to understand the zinc refining process to

obtain a better idea of the compositions contained in zinc waste. The processes of zinc refining [12] are shown in Fig.2.8.

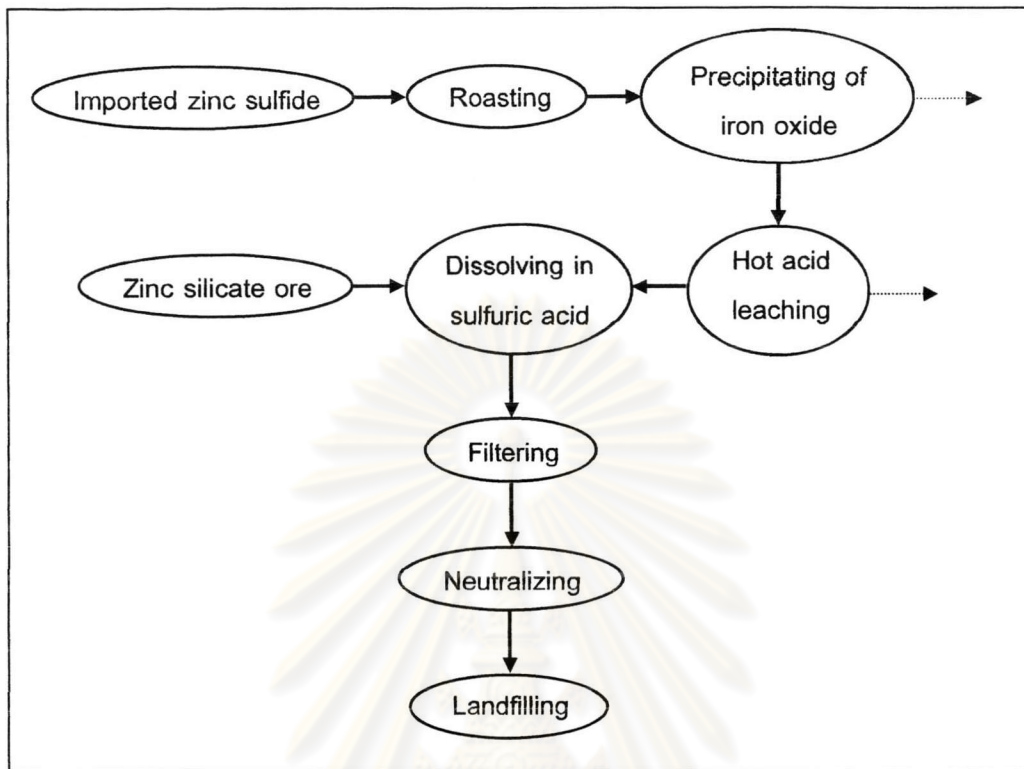


Fig.2.8 Zinc refinery process diagram

Only the treatment process of zinc waste will be discussed in this study.

(A) Zinc sulfide has been imported to use as a raw material together with zinc silicate ores, which are found in Tak.

(B) Concentrated zinc sulfide is then roasted resulting in zinc Oxide (ZnO) and zinc-iron oxide compounds (ZnO.Fe₂O₃).

(C) These compounds are dissolved in sulfuric acid (H₂SO₄) to precipitate iron oxides and other impurities from pure zinc sulfate solution. This process is called neutral leaching. The solution is then separated by electro-winning, resulting in high quality zinc metals through the process R, S, T and so on.

- (D) The precipitated iron oxides and impurities are dissolved in hot concentrated sulfuric acid to remove metals from neutral leaching process. This is called the hot acid leaching process.
- (E) Zinc silicate ores are ground to fine powder
- (F) Ground zinc silicate ores and impurities from hot acid leaching process (D) are dissolved in sulfuric acid together.
- (G) The products from the leaching process above are filtered by using belt filtering process to separate zinc waste from zinc sulfide solution, which came from the addition of zinc silicate ores.
- (H) Zinc waste, which includes iron oxides and other impurities, is neutralized by adding limestone (CaCO_3) to prepare for landfilling.

It is predictable from the treatment process of zinc waste that it contains a high percentage of sulfur dioxide (SO_2), which comes from sulfuric acid. Silica from zinc silicate ores and calcium oxides from limestone can also be shown as main compositions in zinc waste.

2.5 Literature survey

In recent years recycling of industrial wastes has been studied by many scientists around the world. Because environmental, economical and social problems are concerned, the development of useful materials obtained from recycling of industrial wastes becomes very important. It has been shown that recycling of industrial wastes to cement matrix form, i.e. ordinary Portland cement, require an inexpensive thermal treatment process to stabilize hazardous waste in the matrix. The final product is shown to be environmental friendly, which usually passes the regulation of TCLP test. However it has been found that the volume of cement matrix is higher than the waste itself, which reduces the capacity of landfill and the cement mix with toxic waste is not applicable for reuse in the building industries. Accordingly, glass and glass-ceramic technologies are considered to be the most appropriate technologies to immobilize heavy metals in the

stable glass matrix with a consistent reduction of volume and the destruction of organic matter associated with the wastes during glass processing [1].

In Europe, the production of zinc generates a large amount of inorganic waste including goethite and jarosite waste. These wastes are classified as hazardous wastes because they contain high percentage of toxic heavy metals such as zinc, lead, copper, cadmium, and mercury. Most of zinc industries in Europe, which are located in Italy and Spain, use the jarosite process. In 1998 Mario Pelino has studied recycling of jarosite waste in the production of glass and glass-ceramic materials. Jarosite has been used as raw materials with other wastes in order to achieve the proper compositions for vitrification and crystallization under controlled thermal treatment to produce glass-ceramics. This waste consists of a complex composition which is able to be converted to glass-ceramic at low cost with properties suitable to allow commercial exploitation as building materials in the form of paving tiles wall, glass fibers and coloring pigments for ceramics [2, 3]. Basic properties of obtained jarosite glass ceramics have been investigated. These properties depend on type and percentage of crystal phase formed along with the composition of the residual glass. Thus the degree of crystallization has been evaluated and also the kinetic phase formation has been investigated. The leaching resistance of obtained glasses was tested for land-fill disposal as inert material by TCLP test. Degree of crystallization has been studied by density measurement as a function of the thermal treatment schedule [13]. Kinetic phase formation has been investigated both isothermally and non-isothermally by using helium-displacement pycnometer and DTA measurement. The Avrami kinetics and the activation energy of crystal growth were determined [14]. In order to convert jarosite waste to valuable glass-ceramic materials, the chemical durability has been examined based on standard of the United States (US) Environmental Protection Agency (EPA) toxic characteristic leaching procedure (TCLP) test. The TCLP test has been used to evaluate the leach ability of the elements in glass and glass-ceramic samples [4].

Goethite waste (FeOOH) is a hazardous waste derived from zinc hydrometallurgical process similar to jarosite waste but different in compositions. Goethite waste contains many types of oxides including SiO_2 , CaO , MgO , Al_2O_3 with

high percentage of Fe_2O_3 . Preparation and properties of glass-ceramic materials produced by recycling of goethite waste have been studied [15, 16]. Goethite waste has not only been used in producing glass-ceramics by control crystallization of glasses, but has also been used to produce glass-ceramics by using the peturgic method. In this method the melted glass is cooled inside the furnace at a cooling rate of $1\text{-}2^\circ\text{C}/\text{min}$ and upon cooling the nuclei precipitate in a suitable time through crystallization steps then form crystalline phases. Surface and bulk crystallization of glass-ceramics obtained from this method have been studied. The obtained glass-ceramic was black and iridescent surface. The magnetite crystals were found on the surface surrounding by a glassy matrix [5].

It has been found that besides the wastes resulting from zinc hydrometallurgical process, various kinds of inorganic wastes such as municipal solid waste, incinerator fly ash, blast furnace slag, etc. can be used as raw materials to produce glass-ceramics materials. One has studied the possibility of obtaining glass-ceramics from municipal solid waste by sintering crystallization of glass frit. The 100 and 70% of this waste was used as glass-compositions. Phase formation, mechanical and thermal properties were investigated. The chemical stability was characterized by TCLP test. A gehlenite glass-ceramics was obtained and the crystallization was affected by the heating rate [17, 18]. Spanish and Italian coal fly ash as well as Italian municipal incinerator slag have been mixed with glass cullet and dolomite to obtain aluminosilicate and silicate glass-ceramics. The semicrystalline materials were developed by different heat-treatments. The increase of the CaO , Al_2O_3 and Fe_2O_3 with respect to the alkaline oxides resulting from the use of greater amounts of ash or slag causes slight shift of glass-transition and crystallization temperature to higher values, and is favorable to the precipitation of different crystalline phases starting from the surface with the heterogeneous nucleation [19]. Fly ash from municipal waste (MSW) incinerators (as the main raw material) has been mixed with SiO_2 , MgO and TiO_2 to produce glasses, which were then converted to glass ceramics [20].

In general, no matter what kind of industrial wastes used to produce glass-ceramics, either other wastes or glass cullet has been added and mixed together in

different ratios in order to reach the proper compositions for making glasses. For example, a Spanish carbon fly ash has been mixed with glass cullet and dolomite slag to produce glasses then converted to glass-ceramic materials. The nucleation and crystallization kinetic were investigated. The major constituent of the product was gehlenite [21, 22]. The Italian municipal incinerator bottom ash and glass cullet obtained from a community glass recycling program were mixed in three different mixtures and then the ability of these mixtures to be vitrified and devitrified by both bulk and sintering process was investigated by X-ray diffraction, hot stage microscopy, firing shrinkage, water absorption, bulk density measurement and scanning electron microscopy observations. The results showed that high ash content could induce the growth of crystallized fraction volume and the formation of crystal of pyroxene group, and anorthite in addition to wollastonite [23].

Other than bulk glass-ceramic, the glass-ceramic glaze was made from the mixture of granite waste, diopside frit and iron oxide. The effect of iron oxide content on the crystallization of a diopside glass-ceramic glaze was studied. The results showed that the distribution of Fe^{3+} ions among different crystalline phases such as franklinite ($ZnFe_2O_4$) and hematite Fe_2O_3 depends on the iron content in the original diopside mixture. Thus the original glaze crystallizes to franklinite or hematite when iron content is greater than 2 and 15% respectively [24].

It is noticeable that most of the works dealing with recycling of industrial wastes to glass-ceramic materials have studied the leachability of heavy metals by using TCLP test as mentioned previously. That means this test is widely used as a standard to determine chemical stability of each glass-ceramic produced from various kind of hazardous wastes.