Time Resolved X-ray Studies of Crystallization in Zr-based Glasses

by

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Abstract

We have developed new techniques, which enable us to study the kinetics of phase transitions *in situ*. By resistive self heating of samples, heating rates of over 10^4 K/s have been achieved. Our methods allow us to acquire x-ray diffraction patterns as quickly as every 3 ms.

We have used these new techniques of time resolved x-ray diffraction experiments, to study the crystallization kinetics of amorphous NiZr₂, CoZr₂, FeZr₂ and Ni_{36.5}Zr_{63.5}. The experiments were performed at beamline X20C National Synchrotron Light Source.

We have mostly focussed on the crystallization behaviour at high temperatures and therefore faster kinetics. We have found many new results and unexpected metastable phases in these systems. Most of these phases would not be seen using conventional techniques showing the importance of *in situ* time resolved structural measurements to study the kinetics of phase transitions.

Résumé

Nous avons élaboré de nouveaux procédés nous permettant d'étudier m situ les phénomènes cinétiques présents lors des transitions de phase. En utilisant l'effet Joule pour chauffer l'échantillon, nous avons obtenu des vitesses de chauffage supérieures à 10⁴ K/s. De plus, nos méthodes nous permettent d'enregistrer jusqu'à une figure de diffraction toutes les 3 ms.

Nous avons utilisé ces nouveaux procédés de diffraction aux rayons X à résolution temporelle pour étudier la cinétique de cristallisation des matériaux amorphes NiZr₂, CoZr₂, FeZr₂ et N_{12} $_{33.5}$. Nous avons effectué ces expériences en utilisant le faisceau X20C du National Synchrotron Light Source.

Nous nous sommes particulièrement intéressés à la cristallisation à haute température et donc aux phénomènes cinétiques plus rapides. Nous avons obtenu beaucoup de résultats inédits. Entre autres, nous avons découvert une quantité importante d'états métastables présents dans ces systèmes. La plupait de ces états n'auraient pu être découverts sans l'utilisation de méthodes de diffraction *in situ* résolue dans le temps, ce qui montre l'importance de ces méthodes pour l'étude de la cinétique des transitions de phase.

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Chapter 1 Introduction

Metallic glasses, which are in a metastable state, transform either directly into their equilibrium crystalline phases or through a series of stages involving intermediate phases. Crystallization rates depend on temperature, higher temperatures usually having faster rates. An understanding of these transformations is essential, not only for the design of metallic glasses but also for the understanding of the relationship between the characteristics of the glasses and the crystalline phases.

This thesis describes *in situ* time resolved x-ray diffraction experiments of kinetics of crystallization, made possible by the new synchrotron x-ray sources. The challenge of these experiments is to overcome some of the temperature restrictions and to extend *in situ* studies of kinetics of transformations to much faster rates.

This thesis consists of two major parts. The first is the development of the experimental methods. The second is a study of the transformation in several zinconium based metallic glasses.

Before we describe the important aspects of the new experimental methods,

the need for new methods can be understood by reviewing the methods which have been widely used for the studies of the crystallization kinetics. specifically for heat treatments and for structural investigations.

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The studies of kinetics of thermally activated transformations in metallic glasses usually have been done using differential scanning calorimetry, x-ray diffraction and electron microscopy [1-4]. For the most part, the heat treatments have used differential scanning calorimeter. However, the range of transformation rates that can be studied has been restricted due to the inherently low heating rate of this device.

Studies of the structural changes during transformations have been investigated using conventional x-ray diffraction or by electron microscopy using quenched samples. These samples are often produced by differential scanning calorimetry [5]. The necessity of quenching has been due to the long measurement times or due to complicated sample preparation techniques. It is assumed that the structures of the quenched samples are the same as those of the annealed ones [6].

Considering the above methods, the question arises as to how fast a reaction we can observe and how closely the information obtained reflects changes during the anneal as compared to changes during the quench. Answering these questions is one of the motivations of our work.

(i) By increasing the temperatures studied, the range of transformation rate is expanded The interesting question is 'does the crystallization kinetics at faster rates (high temperatures) follow the same mechanisms as those observed at lower rates for the same system?".

•Usually, the reaction rate increases with temperature and therefore higher time resolution is needed for the faster reaction processes so that the measurements will be faster than the total transformation time of the fastest reaction of interest [7]

Since isothermal measurements are inherently easier to analyze, emphasis has been placed on making the measurements isothermally [8]. The heating rate of the sample has to be fast enough to allow the isothermal conditions to be attained before the reaction proceeds very far.

(ii) Do the structures remain the same as observed *in situ* when we quench the sample by using conventional methods [9]? What is the difference in the structures between samples quenched at high rates and slow rates?

Because structural change is what drives the crystallization, confirming the structural evolution during the reaction is important. The investigation of structural change should be performed for the samples with high quenching rates, low quenching rates and *in situ*. Comparison of results with different heating or cooling rates will show the importance of the high time resolution experiments.

Our new experimental techniques allow us to rapidly heat and cool samples while simultaneously acquiring diffractions patterns and permit *in situ* studies at time scales orders of magnitude faster than previously possible..

The second part of this thesis is our results of in situ time resolved x-ray

experiments. Some of the results are in good agreement with previous work, but many of them show unexpected phenomena – Specifically, the appearance of new metastable phases complicates the crystallization kinetics. We can understand the crystallization kinetics in our experiments from both qualitative and quantitative analyses Qualitatively, direct observation of the x-ray diffraction patterns can reveal the appearance of new phases of the system during the transformation – Some of the new metastable phases shown later have been found in this way. The time dependence of the change of peak width of crystalline cubic Fe⁷r₂ was noticed during the run. These observations demonstrate the advantage of real time experiments.

A quantitative approach towards analyzing the crystallization kinetics allows us to trace the time dependence of the volume fractions of the different phases observed in the experimental data. With this informations at different temperatures, interesting physical parameters such as activation energy and Aviami exponents can be derived. The fundamental processes of nucleation and growth can also be examined [10–12]. To find volume fractions, we need more data analysis, that is, fits of the diffraction patterns by an appropriate model. The models are complicated when many phases are involved, requiring many parameters which are each expected to have physical meaning. To fit diffraction patterns for different systems (NiZr₂, $CoZr_2$, $FeZr_2$, $Ni_{36.5}Zr_{63.5}$), we had to set up different models. By using these models, we could measure the time dependence of volume fractions at many temperatures. In some systems, quantitative analyses were able to determine the existence of new metastable phases that were not easily visible by inspection of a single diffraction pattern. Results of our experiments show how crystallization kinetics of many similar systems are different, implying it is not yet possible to predict crystallization kinetics from one similar system to another. Results also show that the resistance change on crystallization is closely related to the phase change.

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In short, while the transformation behavior from metastable to stable systems has been studied extensively there is little information as yet on the structural correlations and their behavior during the progression to the stable state. Time resolved x-ray scattering offers a powerful experimental probe with which to address these issues as it permits us to follow the detailed kinetics of non-equilibrium states by directly measuring the structures [13,14]. To do *in situ* time resolved x-ray experiments, we have used the synchrotron radiation of the National Synchrotron Light Source (NSLS) given by beam line IBM-MIT X20C at Brookhaven National Laboratory.

An introduction to phase transformations is reviewed in chapter 2

In chapter 3, theoretical models of crystallization kinetics, mostly based on the nucleation and growth, are discussed.

Chapter 4 describes one of our main results, the time resolved x-ray experimental methods. The concepts of x-ray scattering, synchrotron radiation and the heat treatments of the samples are presented. Techniques for fast heating and cooling of the samples, and the necessity of high x-ray beam intensities are emphasized. Characteristics of some of the equipment are also discussed.

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Chapter 5 describes the other main part of our work, the results of *in situ* time resolved x-ray experiments. Almost all of the results in this chapter represent new phenomena which had not been observed before. Among the many interesting Zr-based amorphous systems, results for four systems are given.

(i) Our experimental results for $NiZr_2$ at low temperatures demonstrate the advantages of our techniques. It is also shown that the reaction processes at higher temperatures are different from those at lower ones.

(ii) For $CoZr_2$, the existence of an intermediate metastable phase is presented and the results are compared with those using conventional methods.

(iii) For FeZr_2 , the change of particle size is presented as a function of time and the small exponent of the growth law accompanied with coarsening is measured.

(iv) For $Ni_{365}Zr_{635}$, how the phase separation occurs with the appearance of new phase is presented.

The conclusions of the thesis are summarized in chapter 6.

Chapter 2

General Discussion

The purpose of this chapter is to review the general ideas concerning the phase transitions. Some of subjects concerning the phase transitions are defined based on the thermodynamical and statistical point of views. Our main studies, crystallization of amorphous materials, are classified among the different types of transformation classes.

2.1 Phase Transitions

A general phenomenon in nature is the flow of a system from a higher to a lower energy state. Any rearrangement of the atoms, ions or molecules of a system from one configuration to another of lower free energy is referred to as a transformation, reaction or transition [15,16]. Phase transformations can be divided into two classes according to the behavior of derivatives of the free energy (Gibbs free energy) [17,18]. Phase transformations which are accompanied by discontinuous change of state (first derivatives of free energy is discontinuous) are called first order phase phase transformations. Phase transformations which are accompanied by a continuous change of state (higher order derivatives of free energy is discontinuous) are called second order phase transformations. In a first order phase transformation, the reaction is expected to be either a nucleated process or a spinodal process, depending on whether the initial phase is metastable or unstable [19]. Crystallization of amorphous materials in this thesis are concerned with first order phase transformations, prepared initially in a metastable state.

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During the transformation, at least two phases are involved in the procession, the parent and the product phases. The product of a transformation does not have to be a stable state. It can be another metastable state of lower free energy than the first. It is possible for this product to then undergo a further transformation to a more stable configuration and this sequence may be repeated until the most stable form is reached. Here, we distinguish between metastable and stable states as follows [20]. A body in a metastable state is stable within certain limits, the bor¹y will leave sooner or later for another state which is stable, corresponding to the greatest of the possible maxima of entropy. A body which is displaced from this equilibrium state will eventually return to it. Our samples, amorphous materials, are in metastable state. Therefore, during the crystallization, there is a possibility for the initial state to transform into another metastable state before the stable crystalline structures are achieved.

There are three basic types of transformations in solids, based on comparing the phases before and after transformations [21]. (i) change of structure, (ii) change of composition and (iii) change of degree of order. Examples of change of structure are freezing or melting of a substance and crystallization. With respect to change of composition, compositions during the transformation can be represented as the form $C_x \rightarrow C_1 + C_2$, where C_x is a composition before transformation, C_1 and C_2 are the compositions after the transformation. An example of change in degree of order is β -brass (CuZn) [22]. In this alloy the atoms in the crystal above a critical temperature T_c are randomly arranged and below, T_c , the atoms are arranged in an ordered pattern. Phase transformations can occur through one of the above three basic types. But most transformations in alloys are combination of two or more of the basic types. Crystallization of amorphous materials in this thesis are type (i) or a combination of type (i) and (ii), depending on the amorphous compositions.

2.2 Transformation Mechanism

Phase transformations can be homogeneous or heterogeneous [15]. In a homogeneous transformation, with a homogeneous buildup of fluctuations in composition, there is no sharp surface boundary and the surface free energy is small. The trans-

formation occurs throughout the whole system from an unstable initial state such as in spinodal decomposition. In a heterogeneous transformation, there are some transformed or distinguishable regions from the parent phase during an intermediate stage. This region of difference might be a small nuclei or a local fluctuation of the product phase and it is most probable that the transformation will start from these regions. This thesis is primarily concerned with crystallization of amorphous materials which are heterogeneous transformations. Some subjects which are concerned with transformations from metastable to a stable phases will now be described.

2.2.1 Driving Force, Reaction Rate and Activation Energy

The driving force for a transformation is the difference in free energy between the final state and the initial state. This difference has to be negative to have a positive driving force and lead to a possible transformation. A free energy diagram is sketched in Fig. 2.1 [23]. The free energy difference of two minuma, where the upper minimum is in a metastable state and the lower minimum represents the stable state, shows the driving force. The driving force for the reaction to proceed is a function of temperature. For example, in a supercooled liquid, driving force is related to the thermal undercooling below the equilibrium transformation temperature. In the crystallization of amorphous materials, it is related to the anneal temperature. For both cases, the driving force increases with decreasing temperatures. We can expect that it is easier for the system to transform into a stable state when the system has

a larger driving force and usually it has a higher reaction rate. But the reaction rate, which is the transformed volume fraction per unit time, is not just determined by the driving force. The reaction rate is also related to the atomic diffusion or mobility which decreases with decreasing temperature. Therefore the reaction rate is determined by the combination of these two quantities. The competition of these two quantities at a given temperature mostly determines the reaction rate. The final effect is represented as a C-curve [24] in the time temperature coordinate and it will be described in detail, in conjunction with time-temperature-transformation diagrams later, in chapter 3.

All metastable states have a finite driving force tending to produce transformation to a more stable state. Also any transformation path from a metastable state to a lower free energy state has to pass through a higher free energy state during the transformation. Fig. 2.1 is a configuration having two minima which are separated by one maximum. The free energy of an atom or group of atoms increases to maximum and then decreases toward the final value during the transformation. The maximum state in the free energy diagram is called the activated or transition state. The free energy difference from transition state to initial state is called the activation energy for the reaction. At any instant, the elements in the system have a wide spectrum of energies and those elements which have enough energy equal to or larger than the activation energy transform into another state. Those which have insufficient energy to overcome the energy barrier can not transform until they obtain enough energy. The activation energy is widely used to determine the stability of a metastable system, those having high stability have a higher activation energy [25-28]

2.2.2 Nucleation and Growth

If a substance is in a metastable phase, it will sooner or later transform into another phase which is more stable. The new phase is produced by nucleus creation of the product from the parent phase or by growth of an existing particle.

During nucleation and growth, the amount of the new phase changes but usually the cluster shape doesn't change. The shape is determined by how the surface energy is minimized. The shape can be a sphere as in a liquid or isotropic solid or have flat facets as in a crystalline solid or have paraboloidal shapes as in dendritic growth.

The atomic procession from the parent to the product phase is similar to a chemical reaction and for this reason, as a first approximation, the chemical reaction rate equation is sometimes used to describe the transformation kinetics [16]. Growth follows nucleation by atoms jumping across the interface. This causes the grain to grow and the interface to migrate. In this manner the transformed volume increases with time.

There are many kinds of phase transformations like solidification, dissolution, phase separation, evaporation, sublimation, grain growth, where diffusion plays an important role (a typical example of a transformation which is diffusionless is a martensitic reaction). The interfacial movement can be controlled by different conditions of diffusion. There are two typical examples of interfacial movement often used on the transformation kinetics, one is diffusion controlled growth and the other is interface controlled growth. In diffusion controlled growth of a cluster, the radius grows with the square root of time and in interface controlled growth the radius increase linearly with time (constant growth rate) [15,29]. When diffusion is rapid, the concentration of the mother phase is nearly constant and the rate of particle growth is controlled by the interfacial procession, whereas for rapid interfacial reaction the concentration profile is determined by diffusion.



reaction coordinate

Figure 2.1: Free energy profile between two states. E is an activation energy and A is the transition state. The high and the low minima represent the metastable and the stable states, respectively.

Chapter 3

Kinetics of Crystallization

3.1 Introduction

The purpose of this chapter is to present the characteristics of metallic glasses, the different kinds of crystallization processes and the existing theories of nucleation and growth (crystallization of amorphous materials occurs by nucleation and growth process). Some empirical and theoretical laws of the kinetics of crystallization are also described.

The crystallization process includes the preparation of quenched samples, formation of nuclei and the growth of crystals. The individual processes are complicated by various steps. The crystal volume may grow by an increase in the dimension of single nuclei or by the birth of new nuclei. Crystallization of metallic glasses involves the growth of many nuclei and the final crystalline form is a polycrystalline state. The crystallization kinetics as a whole is governed primarily by the degree of annealing of the metallic glasses. The relationship between degree of annealing of the sample and crystallization rate is described by the time-temperature-transformation (TTT) diagram [30]. Different elemental compositions of metallic glasses demonstrate different ways of nuclei formation and growth, resulting in vastly different crystallization processes.

In short, the crystallization kinetics can be affected by many factors such as sample shape and size, homogeneity of the samples and annealing environments. Specifically, the transition mode appeared with the variation of the annealing temperature results the dramatic change of the crystallization kinetics.

3.2 Metallic Glasses

Most of the characteristics of metallic glasses are related to the absence of lattice periodicity. The field of metallic glasses, which were first made in 1959 [31]. has developed rapidly since middle of the 1970's [28,32,33]. Very high cooling rates from the melt (larger than 10^6 K/s [28]) have enabled the formation of glasses from many kinds of binary alloys, many of which exhibit properties which are not found in conventional fabrication methods [27]. This field is not merely an area of pure scientific research. Many new materials have been developed for industrial applications. Outstanding mechanical, magnetic, electrical and chemical properties have initiated the technical and scientific interest in metallic glasses [34]

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. مۇرا The mechanical properties such as strength and ductility can be improved as in Fe-Si compounds. These properties are influenced by alloying and heat treatments. For example, their high hardness and lack of grain boundaries present excellent cutting edges for cutting tools such as razor blades. Several kinds of springs are also made from metallic glasses [35-38].

One of the industrial applications that depends on magnetic properties is for transformer cores. Because of the low magnetic loss, metallic glasses such \sim Fe₇₈ \mathcal{B}_{13} Si₉ offer the opportunity to reduce the core losses in distribution transformers [39,40].

The chemical properties qualify metallic glasses as corrosion resistant alloys for several purposes in chemistry, medicine and industry. For example, the presence of Cr or P in some metallic glasses yields better corrosion restance to salt water or sulfuric acid than that of stainless steel. Here, chromium enriched surface films act as a barrier against the penetration of sodium and zinc [41,42].

Metallic glasses show a large electrical resistivity comparable to crystalline resistance alloys and they have a very small temperature coefficient. These electrical properties favor metallic glasses for use as precision resistors and resistance heaters [43].

Ideally, metallic glasses do not have any crystalline structure. In reality, many different kinds of impurities such as vacancies or different elements can be incorporated from the fabrication process and initiate crystallization. Substitutional and interstitial impurities can lead to preferred sites for nucleation during the cooling

The cooling rate and various material properties have been suggested as significant factors which affect the tendency of liquids to form glasses [44,45]. The amount of crystalline material formed during rabid cooling depends on the cooling rate. A large change in crystal volume fractions will occur with lower cooling rates. In realty it is hard to define or to measure a definite cooling rate to avoid the formation of any nuclei during quenching because measuring the transformed volume is limited by existing experimental techniques. Whatever the case, the question is not whether a material will form an amorphous solid when cooled from the liquid state but how fast should a given liquid be cooled in order that detectable crystallization be avoided [24,46]. Amorphous material so made have to be examined to see the quality of the structure. There are several ways to evaluate the quality of melt spun amorphous materials. It has been generally accepted that transformed volume fraction can be measured roughly as low as 10^{-3} by x-ray diffraction and 10^{-6} with electron microscopy [27].

We used x-ray and differential scanning calorimetry (DSC) to check the quality of our metallic glasses. The absence of crystalline scattering from the x-ray diffraction profiles and seeing no unexpected exothermic peak in differential scanning calorimetry data are good indications that a sample is a structurally homogeneous amorphous phase.

3.3 Classification of Crystallization

Crystallization has been observed to occur generally by nucleation and growth processes. Crystallization processes are different depending on composition and are often complicated by a change in composition between parent and product phases [17]. Metallic glasses may transform either directly into their stable crystalline phases or through many intermediate metastable phases and the transition from one phase to another can generally proceed by some sequence of the following reactions as defined by Köster [48] ypical crystallization reactions are shown schematically in Fig. 3.1 for three compositions of Fe-B metallic glasses. In the following definitions of transition modes, the compositions not labeled 'amorphous' represent a crystalline phase.

Polymorphous crystallization:

This transformation occurs from the metastable metallic glass to another metastable or stable state without any change in local composition. Examples are solidification of pure liquids, allotropic changes in pure metals, crystallization of amorphous NiZr₂, CoZr₂ and Fe₃B [3,49].

 $(\text{amorphous-NiZr}_2) \rightarrow (\text{NiZr}_2)$

 $(amorphous-Fe_3B) \rightarrow (Fe_3B)$

Eutectic Crystallization:

Two different crystal phases appear simultaneously during this transformation.

Usually longer reaction times are needed when compared to polymorphous reactions where separation of components does not have to be considered. Crystallizations of the amorphous $Ni_{36} {}_5Zr_{63} {}_5$ and crystallization of the amorphous $Fe_{80}B_{20}$ are expected to be examples.

 $(\text{amorphous-Ni}_{36\ 5}\text{Zr}_{63\ 5}) \rightarrow (\text{Ni}\text{Zr}_2 + \text{Ni}\text{Zr})$

(amorphous-Fe₈₀B₂₀) \rightarrow (α -Fe + Fe₃B)

Primary Crystallization:

During this reaction, particles of one crystalline phase, which have a different composition from the matrix (parent phase), are produced. This requires the matrix to change composition. Subsequently the matrix transforms into another phase or phases. This transformation may be by one of the three crystallization mechanisms now defined. An example is the production of α -Fe from amorphous Fe₈₆B₁₄, the reaction process is

(amorphous-Fe₈₆B₁₄) \rightarrow (α -Fe + amorphous-Fe-B)

Most reactions occur by a sequence or mixture of these as shown in Fig. 3.1, which shows many paths all leading to the coexistence of α -Fe and Fe₂B.

3.4 Nucleation

Theoretical understanding of homogeneous nucleation has undergone little modification in the last sixty years. A classical kinetic model of nucleation theory by

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Becker-Döring and others has proved to be qualitatively correct and extremely useful. It is the purpose of this section to examine the various assumptions on which the nucleation theories are based and to study the experimental techniques of measuring the nucleation process for the study of crystallization kinetics.

3.4.1 Introduction

The appearance of a crystalline phase occurs when the atoms or molecules in the amorphous phase have enough energy to overcome the energy barrier separating the amorphous and crystalline phases. The formation of the new phase is concerned with a nucleus which is separated from the parent phase by a boundary. Whether the nucleus is very tiny crystallite, a stable complex of ions or molecules or a thermodynamic fluctuation, it is capable of further growth and the transformation can be considered to nucleate on these sites. Whatever the initial structures are, the formation of nuclei is characterized by a nucleation rate. The nucleation rate is defined as number of nuclei of product phase formed per unit time per unit volume of parent phase.

Nucleation and growth is a heterogeneous transformation. Nucleation can be homogeneous or heterogeneous. In homogeneous nucleation, the reaction occurs randomly throughout the whole system and any small volume element in the old phase is chemically, structurally and energetically identical with every other element. Even though it is hard to imagine the ideally homogeneous system, this theory has been applied to many transition phenomena and works well as a first approximation. In heterogeneous nucleation, the transformation occurs at certain preferred sites. These sites could be surfaces, grain boundaries, dislocations, impurities or imperfections.

There are two regions of nucleation theory. One is called steady state nucleation (classical nucleation) and the other is transient nucleation (in which the nucleation rate evolves in time). As detailed in chapter 4, metallic glass samples were prepared, taking every precautions to avoid impurities and inhomogeneities in order to minimize the number of heterogeneous nucleation sites. We will show transient nucleation theory fits our experimental data in chapter 5.

There are few ways to measure the nucleation rate [50]. Optical or electron microscopes can be used to determine the nucleation rate by studying morphology. In these methods we make the volume of product phase discrete and measure the number of particles and their sizes for a given volume of the product phase. The measured number of particles and their size distribution for different times can be used to determine the nucleation rate. One selects the volume randomly and normally assumes the growth rate of nuclei is the same even when they are formed at different times. The other way to measure the nucleation rate is to use the relationship between the overall reaction rate and the nucleation and growth rates. Here the growth rate is measured using an optical or electron microscope first and then this growth rate is used to determine the other parameter, the nucleation rate.

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The results of our *in situ* time resolved x-ray experiments for nucleation and growth are shown in chapter 5. There, the transformed volume fraction of the crystallization of amorphous $NiZr_2$ is obtained by using the transient nucleation theory combined with a constant growth rate.

3.4.2 Classical Nucleation

A review of classical nucleation theories is useful since most other nucleation theories are based on these ideas. Also classical models of nucleation provide a useful insight into the mechanism of decay of the metastable state [23,51]

Early the ries of nucleation were usually formulated in the language of the gas-liquid transition [52]. In the kinetics of new phase formation, a substantial supersaturation of the parent phase is required in order to provide the sufficient size of liquid droplet necessary for initiation of the growth of the new phase. The microscopic fluctuations proposed to drive the transition are the evaporation and condensation of molecules of the gas onto clusters. The clusters are imagined to be embryos from which droplets of the liquid phase may grow upon the accumulation of enough molecules. For a general phace transition, the concepts of evaporation and condensation must be replaced by the appropriate class of microscopic fluctuations which can lead to the product phase from parent phase.

Among the many classical nucleation theories [23,53,54], Becker-Döring [55] theory has been widely reviewed because it gives a concise idea of the nucleation process and predicts the degree of supersaturation required to nucleate liquid droplets. Becker-Döring developed a theory for the rate of homogeneous nucleation of liquid droplets in supersaturated vapors. The assumption of their theory is that the time evolution of a droplet is due to an evaporation or condensation mechanism in which a droplet of certain size gains or loses a single molecule. Effects such as the coagulation of two droplets are not considered. The nucleation rate I they predict is

$$I = K(T)^{-0.5} \exp\left(-\frac{\Delta G_c}{k_B T}\right)$$
(3.1)

where K is a constant related to the atomic frequency factor and ΔG_c is the activation energy for the formation of a critical nucleus which can be described as follows.

The creation of an interface costs energy so that when the nucleus is below a certain size it is unstable and tends to disappear. A nuclei whose size are above a definite value, called critical size, tend to be stable. The nuclei of this size are referred to as the critical nuclei [23,56]. Once the size reaches the critical size, the nuclei proceed to grow, forming grains. Usually a nucleus refers to a cluster of the new phase smaller than the critical size and the term grain describes a cluster larger than the c_1 – cal size [10-12].

The free energy of the critical nucleus can be calculated approximately using values of the macroscopic surface tension and bulk energy of new phase. The simple assumption is that all the nuclei are spread throughout the whole system uniformly

and that the free energy of formation depends on the size and shape of the nuclei. The shape is determined by the surface free energy and is often considered spherical. The formation free energy ΔG of a nuclei of the product phase in the parent phase is [57-59]:

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma \tag{3.2}$$

where ΔG_{ν} is the free energy difference per unit volume from parent to product phase and σ is the surface free energy of a nucleus per unit area which is positive. ΔG_{ν} is negative since the product phase has lower free energy than that of parent phase. It is the free energy cost of the surface which provides the barrier requiring the nucleation process for droplet formation. The maximum of the free energy occurs for nuclei of radius [60-62]

$$r_c = -\frac{2\sigma}{\Delta G_v} \tag{3.3}$$

And the resultant free energy is

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$$\Delta G_c = \frac{16}{3} \pi \frac{\sigma^3}{\Delta G_v^2} \tag{3.4}$$

Usually we can consider $\Delta G_v \propto (\text{T-T}_m)$ where T_m is the melting temperature and T is the temperature of the system [63-65]. When the temperature of the system increases, the critical nuclei size becomes larger. It becomes infinite at the melting temperature where the formation of nuclei does not happen since the parent phase is stable.

Classical nucleation theories often do not apply to real systems [66,67]. It is known that by its physical nature the nucleation process has a non-steady state (transient state) characterized by a time lag [68-70]. However, we can apply those theories to the real systems where the formation of nuclei do not require many atoms or for the early time reaction of the large systems without considering the transient regime of nucleation [64].

3.4.3 Transient Nucleation

In real systems, there is a transient regime in which the nucleation rate increases until it reaches its steady state value. Thus the nucleation rate must be a function of time. The main impediment to nucleation is the time required to grow embryos. This time lag has been studied by many people using more developed theories and have been applied to real systems [48,50,71]. Thus, during the initial transient, we must expect that nucleation rates are far below the results given by steady state nucleation theories.

One of the early works on time dependent nucleation theory was conducted by Kantrowitz [72]. The nucleation rate he derived

$$I_{S} = I_{st} \left[1 + 2 \sum_{m=1}^{\infty} (-1)^{m} \exp\left(-\frac{m^{2}t}{\tau}\right) \right]$$
(3.5)

where τ is the time lag which is expected to increase significantly with decreasing temperature. I_{st} is the steady state nucleation rate which is given by classical nucleation theory [73] in Eq. 3.1. This equation converges rapidly for large times. Using the Poisson summation formula the series can be put into a form which
converges much more rapidly for small t. We get

$$I_{S} = I_{st} \left(\frac{4\pi\tau}{t}\right)^{\frac{1}{2}} \sum_{m=1}^{\infty} \exp\left(-\frac{\pi^{2}\tau}{4t}(2m-1)^{2}\right)$$
(3.6)

To have large rates of nucleation, we have to have t of order τ . It is interesting to truncate Eq. 3.6 at the first term (m=1). It is seen then that transient nucleation time is given by a diffusion like equation for flu "uations from the parent phase to reach the critical nucleus radius [72].

For numerical work, only the first few terms are needed providing Eq. 3.5 is used for times larger than τ and Eq. 3.6 for times smaller than τ . At time $t=\tau$, both give equal results. These two equations will be used to fit our data in chapter 5 [13].

3.5 Reaction Rate

3.5.1 Basic Equations

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The isothermal kinetic processes of crystallization of amorphous materials are too complicated to solve the problem explicitly throughout the whole range of the transformation. However, there has been an empirical equation which describes heterogeneous reactions. The general form of this is [25,74–77]

$$\frac{dx}{dt} = kt^{n-1}(1-x)$$
(3.7)

where k and n are constant during the reaction assumed independent of time at constant temperature and x is the transformed volume fraction. The (1 - x) term reflects the gradual decrease of reaction rate as the unreacted matrix is depleted. The rate constant k and the time exponent n are the useful phenomenological parameters providing a description of isothermal reaction kinetics. The meaning of these constants will be further described later in the discussion of the theoretical model of crystallization kinetics. The constant k can be often expressed as

$$k = k_o \exp\left(-\frac{E}{k_B T}\right) \tag{3.8}$$

where the prefactor k_o is a constant called the frequency factor and k_B is Boltzmann's constant. When k is expressed this way, it is said to be of Arrhenius type with the activation energy E [78]. Eq. 3.7 has been known to describe the isothermal kinetics of a wide variety of heterogeneous reactions. Many of the theoretical kinetic equations for simple processes may be reduced either actually or approximately to the same form as that equation with a specific value of k and n. Since the kinetic processes of the systems concerned are heterogeneous reactions controlled by nucleation and growth, a theoretical model of the kinetics of transformation can be expected to include the parameters, the nucleation and the growth rate. For the formation of models, in general, it is assumed that: at any time t (i) the reaction rate depends on the number of particles of the product phase which is determined by the time dependence of the nucleation rate I in the inverval 0 to t seconds and (ii) the reaction rate depends on the growth rate of each particle. The growth rate

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depends on the geometry of the particles and each dimensional growth velocity

As shown in the previous section, to get the rate of nucleation, some assumptions were introduced as it is generally impossible to deduce the time dependence of the nucleation rate explicitly. To get the growth rate, a similar situation occurs and it is necessary to make some reasonable assumptions. An example, which will be shown later, will describe how the nucleation rate and the growth rate are given by a simplified model. The model will be used for the analyses of our experimental data as will be seen in chapter 5. It has been found that a wide variety of models give exact or approximate equations of this form in Eq. 3.7, with different values of k and n. People have been using measured values of n to infer what the uncroscopic mechanisms are.

One of the theoretical expressions which is the same as the above empirical equation is the Johnson-Mehl-Avrami equation. The equation has been widely used for isothermal studies of crystallization kinetics and can be written as [8]

$$x = 1 - \exp\left(-(kt)^{n}\right)$$
(3.9)

One of the most simple systems in which to check this reaction equation is one where the concentration does not change from the unreacted matrix to product phase such as in polymorphous crystallization. This equation can be understood in detail by following the authors work. The basic assumptions for modeling the equation under the isothermal kinetics are [8,10]

(i) The reaction is driven by nucleation and growth.

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(ii) Nucleation and growth rates are constant through the reaction.

(iii) The nucleation occurs randomly throughout the system.

(iv) The reaction products form spheres except when, during growth, impingement on other growing spheres occurs.

Following Avrami's derivation for the reaction process is useful in order to understand these assumptions and to apply the nucleation and growth rates to the overall reaction process. The *I* particles nucleated at time t_1 will have grown to occupy a volume fraction $\lambda G^3(t-t_1)^3 I$, where λ is a constant depending on the shape of the growing particle and *G* is the growth velocity assumed to be linear. Therefore the transformed volume fraction during early time, when impingement of crystallites can be neglected, is expressed as

$$V_x = G^3 \lambda \int_0^t (t - t_1)^3 I dt_1$$
 (3.10)

Avrami showed that impingement and depletion of the parent phase can be approximately accounted by the formula [5,10,11,79]

$$x = 1 - \exp\left(-V_x\right) \tag{3.11}$$

This is equivalent to saying that I and G are independent of x and that a term (1-x) in the rate equations accounts for depletion and impingement (as in Eq 3.7). Avrami calls V_x the extended volume. It is defined as the sum of the volumes of all particles divided by the total volume, assuming that the particles never stop growing and that new particles keep nucleating at the same rate in transformed as

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well as untransformed material. V_x can exceed unity. Thus the entire problem of determining the kinetics of reaction has been reduced to finding V_x from Eq. 3.10 in any particular case.

Here are two simple examples of applications of the Johnson-Mehl-Avrami equation. When N nuclei are formed at time 0 and none thereafter, the extended volume is

$$V_x = (Gt)^3 N \tag{3.12}$$

and transformed volume fraction becomes

$$x = 1 - \exp\left(-NG^3t^3\right) \tag{3.13}$$

If the nucleation rate is constant, the extended volume is

$$V_x = \frac{G^3}{4} I t^4 \tag{311}$$

and the transformed volume fraction becomes

$$x = 1 - \exp\left(-\frac{I}{4}G^3t^4\right) \tag{3.15}$$

These are the special cases of the Johnson-Mehl-Avrami equation with Avrami exponents 3 and 4 [11].

Another example of the application of the equation is for a system where the nucleation rate is not constant but a function of time. Also growth mechanisms which depend on dimensionality have to be considered. In these complex processes, the transformed volume fraction is not expressed in a simple form. Moreover, different reaction processes are possible with the same exponent.

We use the time dependent nucleation theory which is shown in a previous section for Eq. 3.11 with a three dimensional growth rate. The final expression for the transformed volume fraction is

$$x = 1 - \exp\left(-G^{3}\lambda \int_{0}^{t} (t - t_{1})^{3}I(t)dt_{1}\right)$$
(3.16)

Therefore, by comparing this equation to our experimental results for the transformed volume fraction, crystallization process can be understood as a nucleation and growth. The result for the crystallization of amorphous $NiZr_2$ are given in chapter 5.

3.5.2 Time-Temperature-Transformation (TTT) Diagram

The most important parameter for the study of kinetics is the temperature. The time-temperature-transformation diagram represents the effect of temperature on a typical reaction [27]. It usually shows an initial and final stage of the reaction with time. Also several different transformed volume fractions can be represented. One of the simplest reaction curves in time-temperature-transformation diagram looks like a C as shown in Fig. 3.2, where the curves represent the time-temperature relationship with the transformed volume fraction x=99% [24]. Often the reaction process is complicated and the shape of the reaction curve is a mixture of many C's.

The incubation time is also determined by the annealing temperature. Somewhere in the intermediate range of temperatures, the incubation time becomes minimum and the reaction velocity is maximum. The least time for a given volume fraction to crystallize results from a competition between driving force for crystallization, which increases with decreasing temperature, and atomic mobility, which decreases with decreasing temperature. This competition gives the C shape The reaction time for a given volume fraction often has an Arrhenius temperature dependence.

Time-temperature-transformation curve can be used to describe the rate of each transformation. The positions of the curves differ from alloy system to alloy system and also change with composition within any specific alloy system. It should be clear that the time-temperature-transformation diagram is in no sense a phase diagram, it has been introduced as a qualitative description of the transformation.

As we will see in our differential scanning calorimetry and m situ time resolved x-ray diffraction experiments of NiZr₂ system in chapter 5, the transformation occurs in a simple manner without any complexity at low temperature, simply from the amorphous to the tetragonal phase. We need just one C-curve to describe the reaction at low temperatures. But at high temperatures, we find another metastable phase is involved in the transformation and two C-curves which represent the different reaction products for two phases have to be introduced.



Figure 3.1: Schematic diagram of typical crystallization reaction in amorphous Fe-B compositions, taken from Ref. [48].

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Figure 3.2: Time-temperature-transformation diagram for the crystallization of amorphous $CoZr_2$ and $FeZr_2$ corresponding to a volume fraction crystallized of 99 %, taken from Ref. [81].

Chapter 4

Experimental Methods

4.1 Introduction

In this chapter, the experimental apparatus and the techniques which we have developed are introduced. The theory of x-ray scattering is also reviewed. With our *in situ* time resolved x-ray experimental method we can get time resolutions much faster than has ever been previously reported [81]. This improvement is essential for the study of fast reactions. Therefore, before the experimental methods are described in detail, we will discuss why high time resolution is required and how the new experimental methods are applied to the study of crystallization of metallic glasses. High time resolution experiments require: (i) fast sample heating and cooling, (ii) fast data acquisition, (iii) fast temperature control and (iv) a high intensity x-ray source. In the first place, we must have a high heating rate in order to satisfy isothermal conditions for the system. Specifically, when reaction rates become faster, a higher heating rate is required, otherwise the reaction might start before the final temperature is reached. By resistively heating the sample in one atmosphere of helium gas, we can get heating rates of over 10^4 K/s and cooling rates of 10^3 K/s.

Secondly, with the ability to heat the sample fast, some parameters will have to be monitored simultaneously and rapidly Examples of such parameters are the temperature and resistance of the sample, incident beam intensity and running time (Fig 4.1). The most important parameters are the scattered x-ray intensities which allow us to monitor the structure of the sample. As far as the time resolution is concerned, decreasing the time to acquire each scattering pattern is the most difficult. By using a position sensitive detector and a special monochromator, we can acquire diffraction patterns as fast as every 3 ms [82].

Thirdly, controlling the sample temperature is challenging. A conventional temperature controller has a large response time (for example, response time = 100 ms for a Eurotherm). With this long time constant, constant temperature is not reached as quickly as we want. We use a pyrometer with a response time of 10 ms to read and to control the sample temperature. The output voltage of the pyrometer is used as a feedback to control the power supply. With this method, we obtain a constant temperature to within one percent.

The next thing that has to be considered is the incident x-ray beam. High

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heating rates and fast data acquisition have to be combined with a high intensity incident x-ray beam. The higher the time resolution, the lower the number of counts we measure for each scattered pattern during each sampling time (Fig 4.2). Because the reaction rate becomes faster for the higher anneal temperatures, the experimental running time becomes shorter. For example, from our data with an anneal temperature of T=653 K, a running time of 400 seconds was enough to study the reaction with each parameter (including diffraction patterns) monitored every two seconds. With the anneal temperature of T=757 K, the running time was two seconds and each parameter was monitored every five milliseconds. The high incident intensity is provided by synchrotron radiation from the National Synchrotron Light Source at the Brookhaven National Laboratory using the IBM-MIT beamline X20C.

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As a last part, some partially transformed samples were quenched from the anneal temperature to room temperature at National Synchrotron Light Source with our high quenching rate. These samples are investigated by x-rays and electron microscopy to measure more completely the structural changes and morphology (Fig 4.3). Slowly quenched samples from the differential scanning calorimeter have been examined by x-rays and the structural changes compared with those of the rapidly quenched ones.

Our new experimental techniques, which have the advantage of simultaneously performing rapid heating of the sample and fast monitoring of the parameters, when coupled with the high intensity synchrotron radiation, allows highly time resolved

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data to be obtained. As will be discussed in chapter 5, the kinetics of crystallization at the high anneal temperatures are sometimes significantly different from those at the low temperatures. Structural investigations using x-rays show that a system which is rapidly quenched from the anneal temperature to room temperature is sometimes different from ones quenched slowly in the differential scanning calorimeter.

4.2 Equipment Setup

For *in situ* time resolved experiments with synchrotron radiation, many pieces of equipment are assembled together. To get an overall idea of the setup, we will describe briefly how the equipment is mutually connected and how they are controlled.

There are two IBM personal computers, for alignment of the incident beam and for control of the experiment. The alignment computer controls the slits which adjust the beam size, the mirror to focus the beam on the center of the sample chamber, the monochromator to select the proper wave length and the spectrometer which orients the sample and detector. Also, it controls the horizontal and vertical position of the table on which the spectrometer is mounted. These equipment are controlled by 32 stepping motors.

As shown in Fig 4.4, the other computer acquires the diffracted intensity via a detector, incident beam intensity via an ion chamber, temperature of the sample via

a pyrometer, voltage and resistance of the sample via voltmeters. It also controls the experimental timing and the heating of the sample.

As shown in Fig 4.4, there is other equipment. These are oscilloscope, cooling system, vacuum pump, helium gas and sample chamber. The oscilloscope is connected to the detector console to watch the evolution of structure in real time. By investigating the x-ray patterns, we can immediately adjust experimental conditions such as the anneal temperature and running time. The cooling system maintains the detector at low temperature (-40° C) to reduce background which occurs by leakage across the detector diode [83]. The vacuum pump evacuates the air from the sample chamber and then we fill the chamber with one atm of high purity (99.995 %) helium gas to improve heating and cooling rates (the heat treatments are described in detail later), also to prevent oxidation of the sample.

Another important piece of the equipment is a ballast resistor. This is used in the electric circuit in series with the sample to minimize the power fluctuation caused by change of sample resistance which happen during the transformation. The resistance is chosen to satisfy a condition, $\frac{\partial P}{\partial R} = 0$, where P is the power and R is the resistance of the sample. By working near this point, the changes in resistance which occur on crystallization have minimal effect on the power applied to the sample and minimize the effect on the sample temperature.

The sample chamber is specially designed for our experiments. It is meant to be mounted on a Huber spectrometer. As shown in Fig 4.4, the five windows are positioned to allow both high and low angle experiments. Each window may be covered by different materials depending on purpose. Beryllium has a large absorption depth ($\simeq 1.4 \text{ mm}$ for $\lambda = 2.1 \text{ Å}[22]$) for x-rays and beryllium windows are used for the incident beam and for the diffracted beam. The absorption depth of quartz is small ($\simeq 0.19 \text{ mm}$ for $\lambda = 2.1 \text{ Å}$) for x-rays and large for infrared light. This window is used to absorb the transmitted straight through χ -rays so as to reduce any background scattering which might occur. It is also used to allow the infrared light to reach the pyrometer which is used to read the sample temperature (The pyrometer will be discussed in a later section). Through the glass windows, the environment near the sample which is located inside the chamber can be examined. Each window covers 20° and the positions of the windows are carefully designed so that there exist a pair for each 20° range from 0 to 180 degrees.

Fig. 4.5 shows view of inside of chamber, a sample manipulator is positioned along the center of the cylindrical sample chamber. At one end of the manipulator, the sample holder is mounted. The size is chosen so as not to touch the surface of the chamber and the cooling pipe. The sample holder can be freely rotated about its axis and we can measure the diffraction patterns in transmission as well in reflection. One end of the sample is attached to a rotating spindle. When thermal expansion of the sample occurs, the spindle rotates under spring tension and keeps the surface of the ribbon in a fixed plane. Electric leads on both ends of the sample are connected to the copper cooling pipe which is tightly mounted to the chamber flange. The copper cooling pipes are for the flow of water or gas. By keeping the temperature at the end of the sample constant, temperature drifts are minimized. This copper pipe is also used as the leads to pass the current to the sample. A teflon pipe completes the water connection without conducting electricity. At the other end of the sample manipulator, a linear vacuum feedthrough is located and it is connected to a dc motor. The motor controls the position of the sample by moving the iod inward and outward. This adjustable mechanism plays an important role in the experiments. Small deviation of the position of the tiny sample from the incident beam path give rise to a big effect on the scattered intensities. By using the dc motor and by measuring the scattered intensities from the sample, we can easily center the sample on the incident beams.

4.3 Sample Preparation

We have performed experiments on several different alloy systems. Since the methods to prepare all the samples are very similar, only the way in which we make our most studied system, NiZr₂, will be described.

NiZr₂ glassy samples were prepared by melt spinning pellets with proper composition. To prepare these pellets, the proper masses of high purity Ni(99.999 %) and Zr(99.95 %) were cut from stock. The Ni and Zr were then melted and mixed under a titanium gettered argon gas atmosphere. The melting process was repeated several times to ensure homogeneity. The correct mass of the mixed Ni-Zr was put in a quartz capillary. Melt spinning was done in 35 kpa helium atmosphere to avoid oxidation and high purity argon gas was used to eject the liquid onto the copper wheel. The tangential wheel speed was 60 m/s and the resulting ribbon size was 1.5 mm wide and about 15 μ m thick. X-ray diffraction experiments were performed to examine the quality of the samples. The lack of any detectable sharp lines in the scattering patterns ensured that the samples are amorphous. Samples were also examined by differential scanning calorimetry and found to agree with previously published crystallization temperatures [84].

4.4 X-ray Scattering

4.4.1 Scattering Processes of X-ray

X-rays, which are radiated from accelerated charged particles, undergo scattering when passing through material substances. The scattering of x-rays by matter results from the combination of two different phenomena: (1) scattering by each individual atom and (ii) interference between the waves scattered by these atoms. This interference occurs because the waves scattered by the individual atoms are coherent with the incident wave, and therefore between themselves [85].

Let us consider a group of atoms arranged in some arbitrary manner and placed in a parallel monochromatic beam of x-rays. Each atom emits a scattered wave which is coherent with the incident radiation. These waves interfere each other and they have an intensity which depends on the direction of observation. This dependence is related to the atomic structure of the object. The scattering from crystals and amorphous substances follows from the law governing this dependence.

The intensity of an approximately parallel beam of x-rays is the flux of energy which crosses a unit surface which is normal to the average ray of the beam in one second. The simplest method to measure it is to determine the number of photons emitted or received per second, either per unit area or per unit angle

The application of x-ray scattering to the kinetics of phase transformation in this thesis is by measuring the change of scattering patterns with time. An example is shown in Fig 4.6. The initially broad amorphous scattering pattern shown at t=32s evolves into a final pattern determined by the structure of the crystalline phase.

4.4.2 Powder Method

The powder method of x-ray diffraction which was developed in 1916 by Debye and Scherrer and in 1917 by Hull is one of the most useful techniques of all diffraction methods.

Our samples are initially amorphous and becomes polycrystalline after the transformation. The x-ray diffraction profiles are therefore like that obtained from a powder The objective of this section is to review powder diffraction and to appreciate the difference between the single crystal method and the powder method in x-ray diffraction experiments. For a single crystal specimen, the various diffractions are obtained either by using the polychromatic radiation or rotating the crystal into the various positions which allow diffracting the monochromatic radiation. In the powder method, the specimen consists of a very large number of small crystals in every possible setting with respect to the incident beam. Just by chance, some of the particles will be correctly oriented and the planes of certain directions will be able to diffract the incident beam. Therefore diffraction patterns can be detected with the monochromatic x-ray beam without rotation of the sample

As with a single crystal, a scattered ray from a powdered sample satisfies the Bragg condition,

$$2d\sin\theta_B = \lambda \tag{4.1}$$

here d is the plane spacing of the crystal for a given orientation, θ_B is half the scattered angle and λ is the wavelength of the x-ray.

One of the useful formulae we need gives the scattered intensity for the chosen Bragg angles with respect to the incident beam. The scattered intensity is

$$I = |F|^2 p \left(\frac{1 + \cos^2 2\theta_B}{\sin^2 \theta_B \cos \theta_B} \right)$$
(4.2)

where I is the relative integrated intensity, F is the structure factor and p is the multiplicity factor. The term $(1 + \cos^2 \theta_B)/(\sin^2 \theta_B \cos \theta_B)$ is called Lorentz-polarization factor. It comes from the effect of polarization of the incident x-rays and the geometry of the scattering. In the powder method, all planes of the same spacing superimpose to the same Bragg's angle because of the randomly oriented small

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crystals in the specimen. The multiplicity factor counts the number of planes. This multiplicity factor is different for different sets of planes. For example, p is 6 for $\{100\}$ planes and 12 for $\{110\}$ in cubic structure.

Sometimes we can measure particle sizes in the specimen. The Scherrer formula is used to estimate the particle size of very small crystallites from the measured width of their diffraction curves. The formula is [22]

$$L = \frac{\lambda}{B\cos\theta_B} \tag{4.3}$$

where L is the crystal size. B is the full width at half maximum of the scattering intensity with scattering angle. $2\theta_B$ is the diffraction position of the peak.

Usually we use wavevectors instead of the scattering angles to describe diffraction. They are used because they are independent of the wave length of the incident beam and the peak position of the scattered intensity from a given compound is always at the same wavevector regardless of the kinds of x-rays used. The relation between scattering angle and wavevector is

$$q = \frac{4\pi\sin\theta}{\lambda} = 2k\sin\theta \tag{4.4}$$

where k is wavenumber of the incident beam. With this coordinate the particle size is represented as

$$L = \frac{2\pi}{\Delta q} \tag{4.5}$$

where Δq is the full width at half maximum of the scattered intensity in the transformed coordinate. This formula can be used to estimate particle size in x-ray diffraction experiments.

4.4.3 Synchrotron Radiation and Beamline X20C

Since almost all our x-ray experiments have been done at the National Synchrotron Light Source(NSLS) at Brookhaven National Laboratory(BNL), we will briefly describe synchrotron radiation and beamline X20C of the National Synchrotron Light Source.

A synchrotron is a particle accelerator used to impart energy to particles in order to carry out experiments. It is used for all kinds of particles and in particular used in electron storage rings. Synchrotron radiation is the electromagnetic radiation that is emitted by charged particles which are moving at relativistic speeds in the circular orbits of the synchrotron.

Since 1946, when the electromagnetic radiation emitted by a synchrotron radiation was first seen at the General Electric Laboratories [86], their importance as a light source has continued to grow [87,88]. Why, nowadays, are the synchrotron radiation so widely used in physics, biology, medical science, chemistry and technology? Synchrotron radiation has two characteristics which cannot be obtained from normal radiation sources. One is the wide range of wavelengths or energies (from 10^{-1} to 10^3 Å) available. With these photon energies, studies of many of the properties of atoms, molecules, solids and biological systems can be accomplished The other is the high incident photon flux. This allows experiments on systems where the ratio of the scattered to the incident beam intensity is too small to use conventional x-rays source [89].

As shown in Fig 4.7 (where the heavy line is beamline X20C), the National Synchrotron Light Source consists of two high intensity electron storage rings. One is optimized for the production of synchrotron radiation in the ultraviolet range and has a maximum electron energy of 700 MeV and 51.02 m circumference. The other is the x-ray ring which is operated at an electron energy of 2.5 GeV with a 170.1 m circumference. The electrons in the storage ring circulate in bunches and the number of circulating bunches can be controlled. The beamline which will be explained later is connected to the ring by an aperture and the radiation is observed along the beamline whenever a bunch of electrons passes the aperture. The speed of electrons are close to that of light and the typical bunch length is 10 centimeters. The photons are thus radiated with a pulse duration of nanoseconds. The repetition rate between bunches which is determined by the number of bunches and the size of the storage ring and is typically around 500 nanoseconds for a single bunch at National Synchrotron Light Source. During our experiments, we measure for times long compared to the pulse rate, for this reason the storage ring radiation can be considered as continuous in time for periods of a millisecond or longer.

The radiation pattern is confined to a forward-directed narrow cone, when viewed by an observer in the laboratory frame. The aperture angles are proportional to mc^2/E , where m is the rest mass of the electron, c is the light velocity and E is

the electron energy [90,91].

A schematic diagram of the beamline for the time resolved experiments is shown in Fig 4.8. The beamline includes focusing mirrors, filters, monochromators and ends at an experimental chamber. The beamline is separated by a thick concrete wall from the storage ring which shields the high energy radiation from the areas accessible by the users and staff of the facility. The distance between the radiation source and hutch is 22 m and the beamline mainly consists of 6 and 8 inch stainless steel pipes. The stainless steel pipe is evacuated (10^{-7} torr) and many instruments are connected to the pipe. Turbo pumps and ion pumps are used to keep the mirror and monochromator in high vacuum. By closing shutters, which cut the incident x-ray beam, one can go into the hutch without damage. An ion chamber is used to measure the incident beam intensities.

Whenever we perform experiments, the first thing that has to be done is to align the beam. A well aligned beam means that the incident beam has a high intensity, is well focused and properly positioned at the center of the spectrometer. Proper beam alignment is mostly controlled by the mirror and the monochromator. Accordingly, from among the many pieces of equipment on the beamline, we will describe in detail the function of mirror and monochromator.

The function of the mirror is to focus the beam on the sample. Without focusing, a large distance implies that part of the photon beam is lost due to its angular divergence. The mirror is silicon coated with platinum and is toroidal with 1 cm and 1.5 km radii. The refraction index of materials for x-rays is less than one and so for small angles total external reflection occurs. By adjusting the four rods, we change the meridional radius and incident glancing angle, allowing us to focus the beam in both the vertical and horizontal directions. Since the size of x-ray source is 0.38 mm horizontal \times 0.12 mm vertical, with an aperture angle of 5 mrad \times 0.23 mrad without a mirror, we would have a beam size of 110 mm \times 5 mm at the hutch 22 meters from the source. This large beam spot decreases the intensity enormously. By using the mirror, we can focus the beam to a size of 1 mm x 1 mm and the increase in the intensity by focusing is nearly 10³ times [92].

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The monochromator selects the desired photon energy by eliminating photons of all energies except those with values within a narrow bandpass. It is located 14 in away from the source. At the energy used (6.0 keV), the monochromator has an energy bandpass of 1 %, full width at half maximum. It is composed of an artificial multilayer structure composed of many alternating silicon and tungsten layers having a period of 23 Å. Since the multilayers have a wider energy bandpass than that of a single crystal, it is used to get a high intensity of x-ray. The monochromator consists of two antiparallel multilayers, one fixed and the other movable. By adjusting the incident angle, the energy is selected [82].

In conclusion, the synchrotron radiation and the optics have been briefly described. We have indicated how we acquire the x-rays and how we achieve the high intensity beam which is crucial for highly time resolved x-ray experiments.

4.4.4 Detector

Even though there are many different types of detectors in x-ray measurements, they are all based on the same fundamental principle, the transfer of part or all of the radiation to the detector where it is converted into some other form of energy more accessible to human perception. One of the conventionally used detectors is the scintillation detector. We have used a position sensitive detector, a semiconductor x-ray detector (referred to as a solid state detector), for our time resolved x-ray experiments. The purpose of this section, by describing two detectors, the scintillation detector and the position sensitive detector, is to explain the reasons we have used a position sensitive detector.

A scintillation detector consists of scintillating material which is coupled to a photomultiplier tube either directly or via light guide. As radiation passes through the scintillator, it excites the atoms and molecules of the scintillator causing light to be emitted. This light is transmitted to the photomultiplier where it is converted into a current of photoelectrons which is then further amplified by an electron multiplier system. Since the recovery time of after each event is short, ideally, each photon is expected to produce a signal on the photomultiplier output. The light output of a scintillator is a function of temperature. But this dependence is generally weak at room temperature. The temperature dependence of dark current, *i.e.* a small current which exists even when the photomultiplier is not illuminated, is also small at room temperature. Therefore a temperature control system is not required and the detector is used at room temperature. This detector could be considered as a single channel detector as it counts the number of photons at a given angle for a given time [93].

The detector we have used for the time resolved x-ray experiments is a position sensitive detector (PSD). It is a photo diode array. In contrast to the photoemission of a scintillation detector, an x-ray photon produces electron-hole pairs in a photo diode and the signal is produced as they discharge of the biased photodiode [83]. The position sensitive detector is a linear array with 1024 detectors or picture elements (pixels) and it is therefore a multichannel detector. Each pixel has a 25 μ m length with a 2.5 mm height and the whole array is about 1 inch long. The pixels can be electronically grouped for the different purposes of experiments, grouping more pixels together gives higher time resolutions. For example, if 16 pixels were put together as a group there will be 64 channels. The scattering intensities can be detected at 64 different angles in nearly the same time. For the high spatial resolution experiments, each pixel is used as a separate channel without grouping and one can adjust the distance of the detector from the sample. For the highly time resolved experiments, we shorten the electronical scanning time (time to scan all the pixels) of the detector arrays by making the array numbers small. It takes 16.1 ms to scan the 1024 pixels and only 2.5 ms when the pixels are grouped by 16 into 64 detectors. For the crystallization experiments, we mostly grouped the pixels by 16. Since the intensity of every pixel is read once during the scanning time, the

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output signal of a pixel is an integrated intensity. These detectors also have dark current, a fluctuating current through the semiconductor junction when voltage is applied. This dark current is temperature dependent. A dramatic reduction can be realized by cooling. The dark current is halved with approximately each 7° C cooled [83]. Cooling temperature in our experiments was -40° C, which reduced the losse due to the dark current.

The position sensitive detector is attached on the 2θ arm of the spectrometer allowing its position and angle to be easily varied. The angle with which the detector can cover depends on how far the detector is away from the center of the sample. For our NiZr₂ experiments, the distance is 108 mm and the angular range is 14° (Fig 4.9). The center of the detector is positioned at 51° in 2θ for this sample. The reason we chose this position is as follows. Before the time resolved $x_{-1}ay$ experiments are performed, preliminary experiments are done with the x-rays and differential scanning calorimetry. X-ray diffraction of crystalline samples which have been fully crystallized in a differential scanning calorimeter were measured at 100m temperature. The proper range of diffraction angles where the Bragg peaks from the crystalline phase are well separated and give high intensities are chosen to get high sensitivity to the structural change during the time resolved x-ray experiments. The scattering patterns of the crystalline and the amorphous phases shown in Fig 1.9 represent higher intensities when compared with those at other angles. The houzontal bar shows the range covered by the position sensitive detector window and

gives the indices (hkl) of the main Bragg peaks.

The control system of the position sensitive detector is the optical multichannel analyzer (OMA) console from EG&G Princeton Applied Research. The output of control system, which has the information on the diffraction patterns, can be monitored not only by a computer but also by a oscilloscope. This gives the possibility to watch the transformation phenomena in real time as the data is collected.

Consequently, using a position sensitive detector in our experiments, by grouping the pixels and by changing the distance from the sample to detector, time and spatial resolution are controlled. An ability to acquire a diffraction pattern in a wide range of angles in a short time enables us to study fast crystallization.

4.5 Sample Environment

4.5.1 Temperature Measurement and Pyrometer

The most widely used method to measure the temperature of an object is a thermocouple. This thermometer is however useful only when the thermal mass whose temperature is to be measured is much larger than that of the thermocouple. This thermal mass can be due to the sample itself or due to the environment in which the temperature is kept the same as that of the sample.

For our heating method, resistively heating a small sample with a high heating rate, a thermocouple can not be used. When we touch the sample with a thermocouple, heat from the surface of the sample diffuses away through the thermocouple junction and the temperature is lowered. There is another reason why we do not use a thermocouple. Ideally, the temperature readin position on the sample should be the same as where the incident x-rays hit. If a thermocouple is used, it is inevitable to get x-ray scattering from the thermocouple. Obviously, some other method has to be used to read the temperature of the sample, one which preferably does not touch the sample.

A pyrometer which uses infrared radiation is the best alternative to overcome the above mentioned difficulties. One thing it is important to do when reading temperatures by a pyrometer is calibration. The calibration process is important not only to get the absolute temperatures of the samples, but also to understand the characteristics of a pyrometer. This process will be described in detail hereafter

A pyrometer measures the radiated power from the material when it is at a certain temperature whether it is a blackbody or not. Emissivity is the quantity which used to scale the radiated power to that of an ideal blackbody. It is dependent on the kinds of material and on the radiating wavelengths. We used a pyrometer from IRCON (series 60) which accepts infrared (wave length $\simeq 2.3 \ \mu m$) and has 1 mm radius focal spot.

Blackbody radiation can be represented by Plank's radiation law [94]

$$E_b = C_1 \frac{\lambda^{-5}}{\exp\left(\frac{C_2}{\lambda T}\right) - 1} \tag{4.6}$$

where E_b is the radiated power from a blackbody, $C_1 = 3.74 \times 10^{-16} watt \cdot m^2$ and

 $C_2 = 1.44 \times 10^{-2} \ m \cdot K$ are constants, λ is the radiated wavelength and T is the temperature of the material. For $\lambda = 2.3 \mu m$ and $T = 650^{\circ} K$, $\exp(\frac{C_2}{\Lambda T}) = 1.5 \times 10^4$. The above equation then becomes simply Wien's radiation law [94]

$$E_b = C_1 \lambda^{-5} \exp\left(-\frac{C_2}{\lambda T}\right) \tag{4.7}$$

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And for a non-blackbody,

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$$E_n = \epsilon C_1 \lambda^{-5} \exp\left(-\frac{C_2}{\lambda T}\right) \tag{4.8}$$

where E_n is the radiated power from the non-blackbody and ϵ is the emissivity of the radiating material. For our sample we do not know the emissivity. Therefore for taking our data we set the emissivity on the pyrometer to some arbitrary value and then use Eq. 4.8 to correct the temperature later, by equating

$$\epsilon_1 C_1 \lambda^{-5} \exp\left(-\frac{C_2}{\lambda T_r}\right) = \epsilon_2 C_1 \lambda^{-5} \exp\left(-\frac{C_2}{\lambda T_p}\right)$$
(4.9)

the left term is the radiated power from the sample with emissivity ϵ_1 at temperature T_r . The right term is the assumed form used by the pyrometer with set emissivity ϵ_2 and corresponding temperature T_p of pyrometer reading. Therefore, if we know the relation ship between ϵ_1 and ϵ_2 , the temperature of the sample is obtained from the reading temperature of the pyrometer.

Thus, the question is how we can get that relationship. For the answer, we will think of this problem in two steps. To make the process clear, let's take an example. First of all, we apply the known transformation characteristics of the crystallization kinetics. The temperature of the sample can be obtained from the time to reach a given transformed volume fraction. We have two experimental data on isothermal crystallization of amorphous NiZr₂ from the differential scanning calorimetry, one is at 630 K and the other is at 640 K. The corresponding incubation time, time lag from t = 0 to t_s where crystallization starts, is 202 s and 91 s (Fig 1.10) The incubation time has a measured Arrhenius temperature dependence.

$$t = t_o \exp\left(\frac{E}{k_B T}\right) \tag{4.10}$$

in this expression, t is the incubation time, E is the activation energy, and t_o is the constant which is usually dependent on the composition. Two constants, t_o and E, can be determined from the above two experimental data. With the calculated value of these constants, once the incubation time is known, the equation allows us to get the temperature of the sample. For example, for one set of time resolved x-ray diffraction experiment of NiZr₂ at National Synchrotron Light Source, the incubation time is 146 s (Fig 4.1) and the derived temperature becomes 634 K.

Secondly, we use Plank's radiation law. During the x-ray diffraction expenment at the National Synchrotron Light Source, the reading temperature of pyrometer was 537 K. From Eq. 4.9, using T_r =634 K, we get

$$\ln \frac{\epsilon_1}{\epsilon_2} = \frac{C_2}{\lambda} \left(\frac{1}{T_p} - \frac{1}{T_r} \right) = 1.785 \tag{1.11}$$

As far as the same samples and the same experimental conditions for using pyrometer are kept constant, the numerical value of Eq. 4.11 is fixed. By inserting this constant

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value, we have

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$$T_r = \frac{T_p}{1 - T_p(2.852 \times 10^{-4})} \tag{4.12}$$

This is the formula used for the N₁Zr₂ system to get the temperature T_r of the sample from the reading temperature T_p of the pyrometer.

To get the right transformation temperature during the experiment, the focal spot of the pyrometer on the sample is set to the same position as the x-ray beam strikes.

4.5.2 Sample Temperature Control

One of the most important experimental challenges in our studies of crystallization kinetics has been the necessity to heat the samples *in situ* in a manner that allows rapid change in the sample temperature as well as control, stability and uniformity.

In general, to reduce the time constant for changing temperature we must reduce the thermal mass of the system and increase the instantaneous power which is applied. Our samples consisting of ribbons produced by melt spinning are typically 1.5 mm wide by 15 μ m thick. The ribbons are resistively heated to the temperatures in the range of 640 K to 800 K simply by passing a current through a 40 mm length in vacuum or in helium.

At steady state, heat generated throughout the volume of the sample is radiated or conducted away at the surface. Thin ribbons of uniform cross section produce a large central region of uniform temperature. The instantaneous power to be applied is limited only by the practical current that is applied. By changing the pressure of the helium atmosphere, the thermal conductivity can be controlled. In the higher thermal conductivity atmosphere, we need more input power to get to the same temperature as that of a lower thermal conductivity. Heating rates obtained typically exceed 10^4 K/s and exceed 10^3 K/s for cooling. These high anneal rates enable us to do the *in situ* time resolved x-ray experiments isothermally at high temperatures. We have defined t=0 as the time when temperature reaches 95 % of final temperature. Sometimes we need to rapidly quench the sample to prevent any continuation of the reaction from taking place so further measurements can be made at a particular velocities and the results are compared with those of *in situ* time resolved x-ray experiments are compared with those of *in situ* time resolved x-ray experiments.

Results of the experiments using the conventional methods (differential scanning calorimetry, x-rays and electron microscopy) and *in situ* time resolved x-ray diffraction methods are the same in many cases. But sometimes they are different, showing the importance of our *in situ* experimental methods.



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Figure 4.1: Interesting parameters "hich are acquired simultaneously. The parameters are from the top temperature, resistance and power across the sample acquired during the crystallization of amorphous NiZr₂. The lowest figure is the incident beam intensity. The sampling time is 1.5 s.



Figure 4.2: X-ray diffraction intensities for different time resolutions. The sampling time of each pattern for the amorphous structure of $NiZr_2$ is 5 ms for the top and 2 s for the bottom.



Figure 4.3: Morphology for the crystallization of amorphous $NiZr_2$ as seen from electron microscope. Top left: the amorphous phase, top right: the partially crystallized, bottom: the fully crystallized phase. The sample was rapidly quenched at the National Synchrotron Light source. The pictures were taken by U. Köster.

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Ligure 14: Schematic diagram of equipment setup,



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Figure 4.5: Schematic diagram of the inside of the chamber.



Figure 4.6: Diffraction patterns during the crystallization of amorphous $N_1Z_{1_2}$ The sampling time for each scattering pattern is 2 s. Crystalline volume fractions are 0.2, 0.4, 0.6, 0.8 and 1 starting from the bottom.



Figure 4.7: National Synchrotron Light Source, Brookhaven National Laboratory.

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Figure 4.8: Schematic diagram of beamline X20C at National Synchrotron Light Source.



Figure 4.9: Diffraction patterns of the amorphous and the stable crystalline $NiZr_2$ phases. The horizontal bar shows the wave number range of the detector window.



Figure 4.10. Isothermal differential scanning calorimetry traces observed during the crystallization of NiZr₂. For each experiment, the incubation times which are shown as a bar just before the crystallization starts are 202 s and 91 s from the top

Chapter 5

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Results and Discussion

5.1 Introduction

In this chapter, the results of time resolved x-ray experiments for the crystallization of amorphous NiZr₂, CoZr₂, FeZr₂ and Ni_{36 5}Zr_{63 5} will be described. Different ways of investigating the crystallization process are also shown. These ways may be the measurements of the resistance change with time, the investigations of the pixel intensity change with time, direct observation of the time evolution of the phases of the system without analyzing the experimental data and the investigations of the volume fractions of phases with time from the measured diffraction patterns. The results of experiments using x-ray diffraction and a differential scanning calorimeter will be shown. The difference between using conventional methods and using time resolved x-ray experimental methods will be discussed. The results of experiments on the crystallization of above four compositions can be summarized as follows. The crystallization process of amorphous N₁Z₁₂ is described in detail. The results at low anneal temperatures demonstrate the advantages of our new experimental methods. At high anneal temperatures, the clear appearance of a new metastable phase accompanies an increase of the resistance during initial times. The activation energy of crystallization, the Avrami exponents are determined and the application of transient nucleation theory to our results works well at low temperatures.

In the crystallization of amorphous CoZr_2 , there exists a new metastable phase between the previously known metastable cubic structure and the stable tetragonal structure. We couldn't find this new phase by x-ray diffraction with the samples which were quenched in the differential scanning calorimeter. This result emphasizes the importance of *in situ* experimental methods

Crystallization of amorphous $FeZr_2$ to the metastable cubic structure is studied. The occurrence of coarsening in the cubic structure is observed. The exponent of growth law is nearly 0.2, i.e. $R \sim t^{0.2}$, where R is the particle size and t is the time.

During the crystallization of amorphous $Ni_{36.5}Zr_{63.5}$, there is a simultaneous crystallization of the tetragonal $NiZr_2$ and the orthorhombic NiZ₁ accompanied with the appearance of another new phase The reaction rate to this extra phase is faster than that of the rate to the expected phases at the initial times.

5.2 $NiZr_2$

5.2.1 Introduction

A number of studies have been undertaken on the crystallization process and the reaction kinetics of Ni-Zr metallic glasses [1,26,45,45,49,95-106]. The attraction of this \sim stem is that glasses can be made over a wide composition range covering continuously from Ni₂₀Zr₈₀ to Ni₇₀Zr₃₀ and small variations of compositions can produce large differences in the crystallization processes [33].

Among the glasses composed of Ni-Zr. the NiZr₂ composition has been chosen as one of the first systems in which to study the crystallization process by many authors because the transformation occurs by changing the structure from the amorphous phase to the body centered 'etragonal crystalline phase without changing composition [102,107–110]. Shown in Fig. 5.1 is the Ni-Zr phase diagram.

This simple reaction process provides the advantage of studying the thermostability of the amorphous phase, the nucleation and growth process during the reaction and the application of the existing formulae to explain the kinetics of crystallization. We have also chosen this system as the first of our *in situ* time resolved x-ray diffraction studies.

Results of our experiments have shown much unexpected information, which is summarized here. First of all, one of the big differences from the previous knowledge of the transformation process is the complexity of the reaction process. The amorphous phase transforms into another metastable phase before the final crystalline tetragonal phase occurs. The appearance of this new phase can be seen clearly at high temperatures to have well defined Bragg peaks.

Secondly, the role of *in situ* experiments has to be emphasized because some of the important information about structural changes may not be detectable, if the samples are quenched with a low cooling rate. One of the methods which has been used by many people to examine the structural changes during a transformation is by using the electron microscope or by conventional x-ray scattering with samples which are quenched from the anneal temperature to the room temperature in a differential scanning calorimeter usually with a low cooling rate. Samples quenched with a low cooling rate may no longer be in the same state as the *in situ* ones

Thirdly, it has been reported that the resistance of the system increases at the initial stages of crystallization [102]. Our results show that this effect is accompanied by the appearance of the new metastable phase.

The results of our experiments will be described in two parts, the reaction processes at low and high temperatures. The results at low temperatures demonstrate the quantitative advantages of our techniques. At high temperatures, we will describe how the reaction processes changes by the appearance of the new metastable phase.

5.2.2 Conventional Crystallization

The studies on the kinetics of time resolved measurements in this section have been done at relatively low temperatures compared with the ones in the next section. The purpose in discussing the low temperature experiments is to show the capabilities of time resolved measurements by comparing with the results of other studies. Altounian *et el.* [45,49,84,102,109] have done systematic studies on the crystallization of many Ni-Zr compositions. Our results of time resolved x-ray experiments on the crystallization of amorphous NiZr₂ will mostly be compared with the results of these authors.

Time Evolution of Scattering Intensities

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Using accurate diffracted intensity data from the different phases expected in an x-ray measurement, we can get information about the phases of the system. By investigating the diffraction profiles, the crystallization kinetics can be studied by determining the amount of each phase as a function of time. The experimental results will be shown later and a model to fit the diffraction patterns will be introduced. The relationship with a theory of crystallization kinetics and transformed volume fraction from our measurements will be also described by using transient nucleation theory.

Considering the structural changes during the transformation, the questions which arise are (i) how the phases of the system are revealed in the x-ray diffraction patterns, (ii) how the contributions of the different phases which may exist at the same time can be distinguished from each other and (iii) how the volume fractions of each phase evolve with time.

The time resolved experiments for the crystallization of amorphous N_1Z_{12} were performed with a knowledge of the phases at the initial and at the final stages of the transformation and therefore of the scattering patterns at the corresponding time. The diffraction patterns during the intermediate stages are a mixture of contributions of these phases as shown in Fig. 4.6

To get information on the structural change during the crystallization, several different methods are used. An indication of the structural change during the reaction can be found by investigating the time evolution of a pixel intensity, that is the intensity at a given angle as a function of time. The variation of the pixel intensity does not give information of the structure directly but each pixel can reveal evidence of changes of phases. On crystallization, the intensity change of a pixel is most sensitive to the structural change when the pixel is at the position where scattering peak is largest compared with the others within a given range of angles and sometimes give us the information of the time when the change of the structure occurs. In the bottom of Fig. 5.2, the intensities of two pixels are selected to show how the crystalline phase develops with time by consuming the amorphous phase. The positions of the pixels, q=2.47 Å⁻¹ and q=2.61 Å⁻¹, are located where we can get the highest scattering intensities from the crystalline and the amorphous phases. As shown in Fig. 5.2, from t=75 s, the intensity of one pixel continuously increases and the intensity of the other one decreases. For all 64 pixels, the intensity changes are similar, *i.e* the rate — change is always positive or negative. Another example shown in the top of Fig. 5.2, where q=2.55 Å⁻¹, shows the same manner of pixel intensity change (the reason why we choose this pixel will be explained in the next section). The simple manner of these changes in the pixel intensities indicates that the system transforms in a simple manner (a more complex change in the pixel intensities is shown in the next section).

The structural change can be seen by a direct observation of the time evolution of diffraction patterns without analysis. A three dimensional plot in Fig. 5.3 shows how the phases change with time. Diffraction intensities of the amorphous phase seen at the initial time is replaced by that of the final tetragonal phase. This picture, which is similar to what we see on the oscilloscope during the experiments, doesn't offer information on the amount of phase change explicitly, but we can see qualitatively how the phases change with time.

Volume fractions can be found by introducing a model to fit the diffraction patterns, using a nonlinear least squares fitting program [111]. As shown in Fig. 5.4, where T=642K, there are three types of diffraction profiles, that of the pure amorphous phase at the initial time, the pure crystalline phase at the final time and a summation of the amorphous and the crystalline phases in the middle stage. A linear combination of the initial amorphous and the final crystalline patterns are seen to be sufficient to fit all the scattering patterns during the transformation without introducing any other diffraction line shape. This implies that just two phases are involved in the transformation. Fig. 5.4 shows four representative diffraction profiles. The symbols represent measured x-ray scattering and the solid lines through them are the results of a fit. Each diffraction profile has been fit with two adjustable parameters. The scattering intensity I(q, t), at time t, is given by a linear combination of the contribution of the amorphous scattering $I_1(q)$ and crystal scattering $I_2(q)$. That is

$$I(q,t) = f_1(t)I_1(q) + f_2(t)I_2(q)$$
(51)

The amorphous and the crystalline diffraction patterns are simply the measured patterns shown for the initial and the final times. The prefactors $f_1(t) = f_2(t)$ are the volume fractions of the amorphous and the crystalline phases at time t and are found to satisfy the condition $f_1(t) + f_2(t)=1$. The two parameter fits work well through out all stages of crystallization. Since the time evolution of the volume fractions depend on the reaction process, the quality of the two parameter fit indicates that no complicated intermediate reaction processes appear. Knowing $f_1(t)+f_2(t)=1$, we can reduce two parameter fit to one parameter fit which makes the model simpler, that is

$$I(q,t) = (1 - f_2(t))I_1(q) + f_2(t)I_2(q)$$
(5.2)

and the results of the fit is the same as shown in Fig. 5.4. In Fig. 5.5, the symbols show the resultant crystalline volume fraction. The volume fraction $f_2(t)$ as a function of time may be fit by Eq. 3.16 with the transient nucleation theory in Eq. 3.5

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and Eq. 3.6 The line in Fig. 5.5 shows how well such a model works at T=642 K. Once the volume fraction reaches 0.4, the fit of transient nucleation theory for crystalline volume fraction breaks down, most probably reflecting the fact that the crystalline growth is being influenced by the finite thickness of the ribbon

These structural studies of *in situ* time resolved experiments at low temperatures show that the crystallization of amorphous $NiZr_2$ occurs in a simple manner, directly transforming from the amorphous to the stable crystalline phases, as has been shown in previous studies.

Avrami Exponents

As mentioned in section 3.5, the theory of Johnson-Mehl-Avrami is useful for the study of the isothermal kinetics of the crystallization of the amorphous phase [112]. For the volume fraction expressed as in Eq. 3.9, the Avrami exponent ncan be measured from the slope of plotting $log(-log(1 - x)) v \epsilon r.s.us log(t)$. It is known that the exponent, when it is uniquely determined, gives information on the conditions of nucleation and growth. As an example, the exponent for a constant nucleation rate and linear growth is 4 and it is 3 for the growth of a fixed number of particles [113]. The exponent is 1 for the diffusion controlled growth of cylinders in the axial direction only [16].

The exponent is derived from the fraction of transformed volume and the corresponding time. And the transformed volume-time relationship could be found by using differential scanning calorimetry, electron microscopy or x-ray diffraction. Thus, the Avrami exponent could be obtained easily by using any of these conventional experimental methods and the uniquely determined value has been shown to be a good parameter to explain the overall kinetics of crystallization

Fig. 5.6 shows that the slope of the Avrami plot is constant. The single value of n is 4.4. The value of this order is for isotropic growth and constant nucleation rate [16].

Electrical Resistance Change

Studies of electrical resistivity on the crystallization of the amorphous materials have been done because they provide one of the simplest yet still informative transition properties of the system [4,114]. Before the results of the resistance measurements of the crystallization of amorphous NiZr₂ are discussed, the general properties of resistivity of the amorphous phase will be reviewed. There are two significant differences between a metallic glass when related to the electrical properties of the corresponding crystal: (i) the resistivity in the metallic glass is usually much larger than that of its crystalline counterpart and (ii) the resistivity of the amorphous phase changes less rapidly with temperature [1]. The reason why the resistivity of the amorphous phase is high and flat, has been understood in terms of the intrinsic topological disorder in the atomic structure of a metallic glass. Since a high degree of disorder already exists in the amorphous phase, the additional disorder induced by the thermal vibration has a little influence on resistivity. As well, the resistivity is already high as a result of the scattering caused by the structural disorder. It has been known that the amount of resistance change has a close relationship with the transformed volume fraction during the crystallization of metallic glasses [114]. The fraction of resistance change is directly proportional to the transformed volume fraction because of the higher resistivity of the metallic glass with respect to that of the crystalline phase. This relationship is most applicable when the resistance change is represented in a simple way during the reaction. This means the transformation kinetics can be explained structurally and mechanically without complexity Crystallization of amorphous NiZr₂ is considered as one of the best systems for this relationship.

The resistance measurement a' relatively low temperature is shown in Fig 57. There is a flat region of resistance where only the amorphous phase exists between t=0 to t=75 s. Since the amount of decrease in resistance comes from the transformed crystalline phase, the fraction of decrease in resistance is ideally proportional to the transformed volume fraction of crystalline phase. For example, referring to the x-ray scattering pattern in Fig. 5.4, the total scattering intensity is the summation of the amorphous and the final crystalline phases. The transformed fractions of crystalline phase is 0.4 at time t=189 s. This transformation-time relationship is depicted in Fig. 5.5. The fraction of decrease of the resistance is nearly the same as that of the transformed fraction at the corresponding time. The behavior of the resistance change in our experiments agrees with that of other studies. This also indicates that the reaction occurs in a simple manner.

5.2.3 Rapid Crystallization

Time Evolution of Scattering Intensities

Before we follow the same steps as in the previous section to investigate the time evolution of structures, let us describe the main result of these experiments. There is another phase which has to be introduced at this point. At high anneal temperatures, there appears a new metastable crystalline phase. This phase is clearly seen to precede the appearance of the stable crystalline phase. A diffraction pattern of this structure is shown in Fig. 5.8 [115]. Because of this new phase, the reaction process must be more complicated and the diffraction patterns are no longer simple. As will be discussed later, the existence of this new crystalline phase explains many problems.

A symptom of the complexity of the reaction can be seen from the intensity change of pixels. In Fig. 5.9, where the position of the pixel which is the most sensitive to the x-ray scattering from the metastable crystalline phase, there is a small increase of the intensity in time interval marked with a bar. When the phase change occurs in a simple manner as for example at T=642 K (Fig. 5.2), this pixel intensity does not increase at early times. The crystalline metastable phase appears at this stage. After this time, the intensity profile is determined by a competition between the amorphous, the metastable crystalline and the stable crystalline phases. As the temperature increases, the contribution of the metastable crystalline phase becomes larger. The results demonstrating this relationships at different temperatures are shown in Fig. 5.10, Fig. 5.11 and Fig. 5.12.

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> As we saw in the previous section, the amount of structural change can be found by applying a model to fit diffraction patterns. We first attempt to fit the diffraction pattern at t=16 s at 667K with Eq. 5.2. The best fit by using this equation is -hown in Fig. 5.13. Clearly it doesn't fit well. This demonstrates that the intermediate diffraction patterns are not the simple summation of the scattering of the amorphous and the crystalline phases. To fit the liffraction patterns of the phase mixture, another line shape must be introduced. The question is 'how to determine the line shape?'.

> As an attempt to determine the extra line shape, assuming we have no knowledge of the metastable phase, we introduce a new line shape to be added to the linear combination of the patterns of the amorpho — and the crystalline phases. Considering this line shape to be composed of peaks and by varying the positions, the widths and the relative intensities of these extra peaks, the diffraction pattern can be fit. The diffraction pattern with the fit is shown in Fig. 5.14 at t=16 s and the extra line shape is represented as solid line. Once the extra line shape is determined, it should be applicable to all the diffraction patterns during the transformation if the overall intensity is scaled. This is shown in Fig. 5.15. This works well for all diffractions patterns and also for different anneal temperatures, suggesting the presences of a new phase which has a diffraction pattern of similar to this line shape. The question is 'what gives rise to this line shape?'. It turns out to be the diffraction pattern of

the metastable phase. The peak positions and the relative intensities we have found by the above method are the same as that of the metastable phase shown in Fig. 5.8.

Now, since we know the diffraction patterns of the amorphous, the metastable and the crystalline phases, we can develop a model to fit the diffraction patterns. In the model, it is assumed that the diffraction patterns are a linear combination of different patterns. The formula used is

$$I(q,t) = f_1(t)I_1(q) + f_2(t)I_2(q) + f_3(t)I_3(q)$$
(5.3)

where I(q, t) is the scattered x-ray intensity at time t. The quantity $I_1(q)$ is the scattering pattern of the amorphous phase, $I_2(q)$ is the pattern of the stable crystalline phase and $I_3(q)$ is the pattern of the metastable crystalline phase. The amorphous and the stable crystalline diffraction patterns $I_1(q)$, $I_2(q)$, respectively are simply the measured patterns shown at the initial and the final stages. The metastable crystalline diffraction pattern $I_3(q)$ is shown in Fig. 5.8, from which we determine the position and relative intensities of the peaks using a Gaussian functional form for each peak. Then we select one scan which has relatively high intensities for the metastable phase. This we fit by adjusting the peak width and volume fractions and by forcing it to satisfy $f_1(t) + f_2(t) + f_3(t) = 1$. This procedure determines $I_3(q)$ for using Eq.5.3. The prefactor $f_1(t), f_2(t)$ and $f_3(t)$ are the volume fractions of the amorphous, the metastable and the stable phases at time t and are found to satisfy the condition $f_1(t) + f_2(t) + f_3(t) = 1$, even though each volume fraction vary freely during the run. Thus, the three parameter fit can be reduced to a two parameter fit The formula is

$$I(q,t) = (1 - f_2(t) - f_3(t))I_1(q) + f_2(t)I_2(q) + f_3(t)I_3(q)$$
(5.4)

In Fig. 5.17 (some of the fitted diffraction patterns are shown in Fig. 5.16), at T=653 K, the volume fractions are shown $f_1(t)$ is plotted as a dotted line, $f_2(t)$ as a solid and $f_3(t)$ as a dashed. The metastable crystalline fraction $f_3(t)$ is small and the reaction process is mainly governed by the loss of the amorphous volume fraction and the corresponding increase of the volume fraction of the stable crystalline phase. As shown in Fig. 5.19 (some of the diffraction patterns are in Fig. 5.18), where T=679 K, the volume fraction $f_3(t)$ approaches 10%. It can be seen the initial loss of the amorphous scattering is taken up just by an increase of the metastable crystalline phase. With higher temperatures (some diffraction patterns and the evolution of volume fraction with time at T=709 K, T=740 K and T=757 K are in Fig. 5.20 and Fig. 5.21, Fig. 5.22 and Fig. 5.23. Fig. 5.24 and Fig. 5.25, respectively), a higher metastable crystalline volume fraction is reached before the conventional phase takes over.

One more question we can ask is 'does the metastable phase exist only at high temperatures?'. For the model used in previous section at low temperatures, we used two patterns, that of the amorphous and the crystalline phases with one adjustable parameter. But close investigation of the fits shows that there exists an extra line shape, although its contribution is small. This has been shown in our previous work [110] Therefore, the metastable phase exists at least in the temperature range 640 K to 800 K, in which our experiments have been performed.

From the structural study and from the investigation of the time evolution of volume fractions, a few facts can be derived. Clearly, the appearance of the metastable crystalline phase initiates the crystallization of amorphous N₁Zr₂. The maximum volume fraction reached by the metastable crystalline phase increases with higher anneal temperature. There is a certain temperature range, where the amorphous phase transforms into the metastable crystalline phase completely and then this metastable phase transforms into the stable crystalline phase thereafter (Fig. 5.8 is the x-ray scattering pattern from a quenched sample with $f_3=1$). The transformation at early times must be considered as a mixture of three different phases. The structure of the metastable phase is as yet not determined and work is continuing to examine this problem.

Previous work has shown that small quantities of oxygen or boron may trigger the appearance of a new phase in NiZr₂ [102]. The oxygen induced phase has a cubic structure which is similar to the cubic structure found during the crystallization of amorphous CoZr₂ and FeZr₂ discussed in the next sections. Crystallization into these cubic phases is always accompanied by an increase in resistance. The structure of the new metastable phase we found in NiZr₂, with x-ray diffraction pattern covered from q=1.4 Åto 5.1 Å, can not be indexed by this cubic structure. The relationship between our metastable phase and the impurity induced phase requires further work It could be studied by systematic measurements of samples with controlled amounts of impurities at high reaction rates.

Avrami Exponents

The way in which the phases evolve with time explains many unsolved problems in the study of kinetics of crystallization of amorphous $NiZr_2$, such as the increase of resistance at the early times of the transformation, the non-uniqueness of the Avrami exponent and the different values of activation energies from other studies. We will now discuss these aspects.

The measurement of an Avrami exponent has been widely used to study the crystallization behavior of metallic glasses. The presence of the metastable phase in the crystallization of amorphous NiZr₂ shows that a single exponent should not be expected. A single value of the exponent exists at low anneal temperatures where the effect of the metastable phase is small as shown in Fig. 5.6 The value of n is 1.1. In this run, where the temperature is 642 K, the amorphous phase transforms into the stable crystalline phase with only a small amount of the intermediate metastable phase.

As shown in Fig. 5.26 for T=653 K, the exponent does not have a single value in the region of transformed volume fraction between 0.02 and 0.4. For low volume fractions n is 5.2 and changes to 4.4 near x=0.18. These values are different from 3.44 measured by Altounian *et al.* [49] based on the use of the differential scanning calorimeter and show it is hard to establish the nucleation and growth process definitely just with the Avrami exponent. Greer [5] summarized a variety of Avrami exponents for the crystallization of amorphous $Fe_{80}B_{20}$, where the exponents vary between 0.4 to 4.87 depending on the experimental method and the range of the transformed volume fractions. By our *in situ* measurements of structure, it is straightforward to see that it is appearance of a new phase which explain the behavior of the Avrami exponent for NiZr₂. The wide variety of possible exponents in the Johnson-Mehl-Avrami equation shows that it is not possible to determine the nucleation and growth behavior of the phase transformation from the data on the time dependence of transformed volume and structural change only. It is essential to have the additional knowledge about the reaction process, possibly obtained from direct microscopic observations of the transforming particle as a function of time [29].

Electrical Resistance Change

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Although it had been previously shown that the resistance of amorphous $NiZr_2$ decreases during the crystallization, the results of the time resolved experiments show that it continuously decreases only at the relatively low anneal temperature and increases during the early stage of transformation at high anneal temperatures. This increase corresponds to the appearance of the metastable crystalline phase.

The amount of increase of resistance becomes larger with the higher anneal temperatures. For example, at T=709 K, as shown in Fig. 5.27, the resistance is increased at first up to approximately 5 % compared with that of the amorphous phase and then it decreases. A larger increase of resistance is shown in Fig 5.28 and

a smaller increase is shown in Fig 5 29. The e increase can be compared with the one discussed in the previous section (Fig 57) where the amount of the metastable phase is negligible.

The obvious question asks why the resistance increases in the early stages of transformation. The reason for an increase of resistance in the crystallization of amorphous NiZr₂ has not been clearly answered except in the case of increasing oxygen content [102]. Recent work on the change in electrical resistance during the initial stages of crystallization of amorphous NiZr₂ [116] has explained the resistance increase by percolation theory. Our interpretation is quite different.

We now see the cause of the resistance increase based on the results of the time resolved x-ray diffraction experiments. The structural study during the transformation shows the crystallization starts when the resistance increases. Referring to the resistance diagram in Fig. 5.27, where T=709 K, the resistance of the sample keeps on increasing from initial to t=0.5 s. The volume fraction of the stable crystalline phase in this time interval is negligible (Fig 5.21). During this time, the volume fraction of the amorphous phase decreases and the crystalline metastable phase appears. The volume fraction \neg f the metastable phase approaches up to 10 %. The amount of increase of the metastable phase is comparable to that of the resistance. This relationship is shown in other experimental data sets (Fig. 5.28 and 5.25, Fig. 5.29 and 5.19). In Fig. 5.29, the resistance increases until t=5 s. In the same manner as the description in above paragraph, only the amorphous and the

metastable crystalline phases have enough volume fraction to affect the resistance (Fig. 5.19).

Accordingly, from the above analysis two important facts for the resistance increase can be derived: (i) the increase of resistance comes from the appearance of the metastable crystalline phase during the early stages of the crystallization and (ii) the resistivity of the metastable crystalline phase is larger than that of the amorphous phase. Therefore, the increase and the decrease in resistance is the result of the competition between the high resistivity of the metastable crystalline phase.

In conclusion, (i) the fraction of decrease of resistance is directly proportional to that cf transformed volume of stable crystalline NiZr₂ phase at low temperature, (ii) the appearance of the metastable crystalline phase is ahead of the stable crystalline phase and (iii) at high temperature, the increase of resistance at the early stage of transformation is caused by the appearance of the metastable crystalline phase which has high resistivity.

Activation Energy

The stability of metallic glasses is important for their applications. The persistence of a metastable glassy phase can be related to an activation energy and the transformation occurs with a rate dependent on temperature. The nucleation rate depends on the magnitude of activation energy [117]. The system will be more thermally stable if it has a higher activation energy and it is the main parameter determining the dependence of the kinetics of crystallization on the other parameters such as time and temperature [26]

There are two main ways to measure the activation energy One is to measure the crystallization temperature T_p at different constant heating rates and the other is measuring the time of crystallization at different constant temperatures The Kissinger method is widely used in differential scanning calorimetry with a constant heating rate [3,77]. It is written as

$$\frac{d\left(\log\frac{\phi}{T_p^2}\right)}{d\left(\frac{1}{T_p}\right)} = -\frac{E}{k_B}$$
(5.5)

in which ϵ divation energy E is given by the slope of a plot of $log\left(\frac{\phi}{T_p^2}\right)$ versus T_p^{-1} , where ϕ is the heating rate and T_p is the temperature at the peak

When the system is kept isothermal, differential scanning calorimetry, electron microscopy or x-rays can be used. But there are limits to each of these methods. Electron microscopy is limited by the local area of observation and differential scanning calorimetry is good when the exothermic peak is simple. Conventional x-ray methods require measurements on many samples. Often the variability between samples is as large an effect as the one trying to be measured

In situ time resolved x-ray diffraction methods compensate for these disadvantages since the small relative changes of structure can be detected in the diffraction patterns. Also the x-ray beam covers a wide area of the sample and the experimental conditions stay constant until the transformation is completely finished. The overall activation energy for crystallization from the *in situ* time resolved x-ray experiments can be measured. Several different experimental data sets which correspond to the different temperatures are used. The measured values of the activation energy are not sensitive to the volume fraction within a certain range of transformed volume fraction

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As shown in the time-temperature-transformation diagram of chapter 2, it takes different times to get the different transformed volume fractions in a given system. For the NiZr₂ system, the time to reach transformed volume fractions x=0.05, 0.95 were measured at different temperatures. They are plotted as a timetemperature-transformation diagram in Fig. 5.30 which shows the relationship for the metastable and stable phases. It can be seen that all the data are still well below the expected up turn (C shape) of the time-temperature-transformation diagram

If the time to reach a certain volume fraction has an Arrhenius temperature dependence then

$$t_x = t_o \exp\left(\frac{E}{k_B T}\right) \tag{5.6}$$

here t_x is the time taken for the transformation to reach the transformed volume fraction x. The constant t_o is dependent on the different compositions and structure [118]. The value E/k_B is the slope in a plot of $log(t_x)$ versus 1/T.

A typical plot is shown in Fig. 5.31 for x=0.25. The measured values of activation energy for cifferent transformed volume fraction are the same within errors. As shown in Fig 5.31, the measured value of activation energy for the appearance of the stable phase is E = 2.2 eV If we try to estimate activation energy for the summation of volume fraction of the metastable and the stable phases (i.e., volume fraction of the amorphous phase is 0.75), as shown in Fig. 5.31, it is 2.9 eV. This value is comparable to that found by Altounian *et al.* [49,84], where E=3.1 eV (E=2.6 eV from Mekamey *et al.* [3]). Our small value can be related to the metastable phase. Since the activation energy represents the stability of formation of the stable phase, a smaller value could represent that the metastable phase may initiate the fast nucleation of stable phase. The value of the activation energy obtained through this method is insensitive to the stage of crystallization, even though the crystallization process is complicated, and it can be understood as an average quantity to describe the overall reaction of crystallization.

In summary, we have seen the experimental results at high temperature as well as those at low temperature. The results at low anneal temperatures demonstrate the advantage of our new experimental methods when compared to conventional methods. A model with one parameter (volume fraction) has been used to fit the diffraction patterns. The transient nucleation theory has been applied to the results of the fit and it works well. These results show that the crystallization process is similar in many ways to what was seen in previous studies.

At high anneal tempe. ures, the appearance of a new metastable phase accompanies the increase of the resistance during initial times. A model with two parameters has been used to fit the diffraction patterns. Because of the appear-

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ance of a metastable phase, the Avrami exponent is not expected to be determined uniquely. Activation energy for the appearance of the stable phase is 2.2 eV

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A close investigation of the data shows that the metastable phase exists in all our data, even at low temperatures. The maximum volume fraction of the metastable crystalline phase increases with higher anneal temperatures. Therefore, the transformation at early times must be considered as a mixture of three different phases: the amorphous, the metastable crystalline and the stable crystalline phases. Transformation of a mixture of three phases may require more than one reaction channel such as: the two step sequence amorphous phase \rightarrow metastable phase \rightarrow stable phase.



Figure 5.1: Phase diagram of Ni-Zr compositions, taken from Ref. [85].

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Figure 5.2: Change of pixel intensity as a function of time during the crystallization of amorphous NiZr₂ at T=642 K. The dotted, the dashed and the solid lines are the scattering intensities of pixels which are located at q=2.61 Å⁻¹, q=2.47 Å⁻¹ and q=2.55 Å⁻¹. Each pixel is sensitive to the x-ray scattering of the amorphous, the stable crystalline and the metastable crystalline phases.



Figure 5.3: Three dimensional plot of *in situ* time resolved x-ray scattering patterns during the crystallization of amorphous N₁Zr₂ at T=653 K. Initial scattering pattern is for the amorphous and the final scattering pattern is for the tetragonal phases. The x, y, z axes are the time, the wave number and the scattering intensity Run time is 400 s and the detector range is from q=2.3 Å⁻¹ to q=2.94 Å⁻¹.



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Figure 5.4: X-ray diffraction patterns during the crystallization of amorphous NiZr₂ for a representative time sequence at T=642 K. Symbols represent measured x-ray scattering and solid line through them are the result of a fit with Eq. 5.1. The dotted and the dashed lines are the x-ray scattering of the stable and the amorphous phases. The times selected are based on the time it takes to reach x=0, 0.1, 0.4 and 1 crystal volume fraction. The time per diffraction pattern is 1.5 s.



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Figure 5.5: The time dependence of volume fraction of the stable crystalline phase at T=642 K. The solid line is a fit with Eq. 3.16 with τ =13.1 s and $G^3\lambda I_{st}$ =3.9×10⁻⁷ s⁻⁴.


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Figure 5.6: Plot of log(-log(1-x)) versus log(t) for the crystallization of amorphous NiZr₂ at T=642 K. The Avrami exponent measured from the slope is 4.4. The points are from a fit using Eq. 5.1. The straight line shows the existence of a single value of the exponent. The transformed volume fraction in the figure carries from 0.02 to 0.4.



Figure 5.7: The time dependence of temperature, resistance and power during the crystallization of amorphous NiZr₂ at T=642 K.

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Figure 5.8: Diffraction pattern of metastable crystalline $NiZr_2$. The sample was quenched at the National Synchrotron Light Source. X-ray diffraction was undertaken by using conventional methods. The horizontal bar represents the range of angles of the detector window at the synchrotron.



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Figure 5.9: Change of pixel intensity as a function of time during the crystallization of amorphous NiZr₂ at T=667 K. The dotted, the dashed and the solid lines are the scattering intensities of pixels which are located at q=2.61 Å⁻¹, q=2.47 Å⁻¹ and q=2.55 Å⁻¹. Each pixel is sensitive to the x-ray scattering of the amorphous, the stable crystalline and the metastable crystalline phases.



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Figure 5.10: Change of pixel intensity as a function of time during the crystallization of amorphous NiZr₂ at T=679 K. The dotted, the dashed and the solid lines are the scattering intensities of pixels which are located at q=2.61 Å⁻¹, q=2.47 Å⁻¹ and q=2.55 Å⁻¹. Each pixel is sensitive to the x-ray scattering of the amorphous, the stable crystalline and the metastable crystalline phases.



Figure 5.11: Change of pixel intensity as a function of time during the crystallization of amorphous NiZr₂ at T=709 K. The dotted, the dashed and the solid lines are the scattering intensities of pixels which are located at q=2.61 Å⁻¹, q=2.47 Å⁻¹ and q=2.55 Å⁻¹. Each pixels are sensitive to the x-ray scattering of the amorphous, the stable crystalline and the metastable crystalline phases.



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Figure 5.12: Change of pixel intensity as a function of time during the crystallization of amorphous NiZr₂ at T=740 K. The dotted, the dashed and the solid lines are the scattering intensities of pixels which are located at q=2.61 Å⁻¹, q=2.47 Å⁻¹ and q=2.55 Å⁻¹. Each pixels are sensitive to the x-ray scattering of the amorphous, the stable crystalline and the metastable crystalline phases.



Figure 5.13: Fit of the t=16 s diffraction pattern for the crystallization of amorphous NiZr₂ at T=667 K. Symbols represent measured x-ray scattering and the solid line through them is the result of a one parameter fit with Eq. 5.2.



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Figure 5.14: Fit of the t=16 s diffraction pattern for the crystallization of amorphous NiZr₂ at T=667 K. The dotted, the solid and the dashed lines are the x-ray scattering of the stable, the metastable and the amorphous phases. Symbols represent measured x-ray scattering and the solid line through them is the result of a two parameter fit with Eq. 5.4.



Figure 5.15: X-ray diffraction patterns during the crystallization of amorphous NiZr₂ for a representative time sequence at T=667 K. Symbols represent the measured x-ray scattering and the solid line through them are the results of a fit with Eq. 5 3. The dotted, the solid and the dashed lines are the x-ray scattering of the stable, the metastable and the amorphous phases. The times selected are based on the time it takes to reach X=0, 0.1, 0.4 and 1 crystal volume fractions. The time per diffraction pattern is 0.5 s.



Figure 5.16: X-ray diffraction patterns during the crystallization of amorphous NiZr₂ for a representative time sequence at T=653 K. Symbols represent the measured x-ray scattering and the solid line through them are the results of a fit with Eq. 5.3. The dotted, the solid and the dashed lines are the x-ray scattering of the stable, the metastable and the amorphous phases. The times selected are based on the time it takes to reach X=0, 0.1, 0.4 and 1 crystal volume fractions. The time per diffraction pattern is 2 s.

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Figure 5.17: The time dependence of volume fraction during the crystallization of amorphous NiZr₂ at T=653 K. The dotted, the solid and the dashed lines are the volume fractions of the amorphous, the stable and the metastable phases, respectively. Those are the result of a fit with Eq. 5.3.



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Figure 5.18: X-ray diffraction patterns during the crystallization of amorphous NiZr₂ for a representative time sequence at T=679 K. Symbols represent the measured x-ray scattering and the solid line through them are the results of a fit with Eq. 5.3. The dotted, the solid and the dashed lines are the x-ray scattering of the stable, the metastable and the amorphous phases. The times selected are based on the time it takes to reach X=0, 0.1, 0.4 and 1 crystal volume fractions. The time per diffraction pattern is 0.2 s.



Figure 5.19: The time dependence of volume fraction during the crystallization of amorphous NiZr₂ at T=679 K. The dotted, the solid and the dashed lines are the volume fractions of the amorphous, the stable and the metastable phases, respectively. Those are the result of a fit with Eq. 5.3.



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Figure 5.20: X-ray diffraction patterns during the crystallization of amorphous NiZr₂ at T=709K for a representative time sequence. Symbols represent the measured x-ray scattering and the solid line through them are the results of a fit with Eq. 5.3. The dotted, the solid and the dashed lines are the x-ray scattering of the stable, the metastable and the amorphous phases. The times selected are based on the time it takes to reach x=0, 0.1, 0.4 and 1 crystal volume fractions. The time per diffraction pattern is 0.05 s.



Figure 5.21: The time dependence of volume fraction during the crystallization of amorphous NiZr₂ at T=709 K. The dotted, the solid and the dashed lines are the volume fractions of the amorphous, the stable and the metastable phases, respectively. Those are the result of a fit with Eq. 5.3.



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Figure 5.22: X-ray diffraction patterns during the crystallization of amorphous NiZr₂ for a representative time sequence at T=740 K. Symbols represent the measured x-ray scattering and the solid line through them are the results of a fit with Eq. 5.3. The dotted, the solid and the dashed lines are the x-ray scattering of the stable, the metastable and the amorphous phases. The times selected are based on the time it takes to reach x=0, 0.1, 0.4 and 1 crystal volume fractions. The time per diffraction pattern is 0.0167 s.



Figure 5.23: The time dependence of volume fraction during the crystallization of amorphous NiZr₂ at T=740 K. The dotted, the solid and the dashed lines are the volume fractions of the amorphous, the stable and the metastable phases, respectively. Those are the result of a fit with Eq. 5.3.



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Figure 5.24: X-ray diffraction patterns during the crystallization of amorphous NiZr₂ for a representative time sequence at T=757 K. Symbols represent the measured x-ray scattering and the solid line through them are the results of a fit with Eq. 5.3. The dotted, the solid and the dashed lines are the x-ray scattering of the stable, the metastable and the amorphous phases. The times selected are based on the time it takes to reach x=0, 0.1, 0.4 and 1 crystal volume fractions. The time per diffraction pattern is 0.005 s.



Figure 5.25: The time dependence of volume fraction during the crystallization of amorphous NiZr₂ at T=757 K. The dotted, the solid and the dashed lines are the volume fractions of the amorphous, the stable and the metastable phases, respectively. Those are the result of a fit with Eq. 5.3.



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Figure 5.26: Plot of log(-log(1 - x)) versus log(t) for the crystallization of amorphous NiZr₂ at T=653 K. The Avrami exponent measured from the slopes are 5.2 for the first straight line and 4.4 for the second straight line. The points are from the fit using Eq. 5.3. Two different straight lines show the exponent is not determined uniquely. Here, x is the volume fraction of the stable phase and the represented value is between 0.02 and 0.4. In this run, the intermediate metastable phase appears.



Figure 5.27: The time dependence of temperature, resistance and power during the crystallization of amorphous NiZr₂ at T=709 K.



Figure 5.28: The time dependence of temperature, resistance and power during the crystallization of amorphous NiZr₂ at T=757 K.



Figure 5.29: The time dependence of temperature, resistance and power during the crystallization of amorphous NiZr₂ at T=679 K.

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Figure 5.30: Time-temperature-transformation diagram for the crystallization of amorphous $NiZr_2$. Circles are for the metastable crystalline and squares are for the stable crystalline phases.



Figure 5.31: Time-temperature relationship for the crystallization of amorphous NiZr₂. The times selected are based on the time it takes to reach x=0.25. The slope is the activation energy from the Arrhenius equation. The activation energy is 2.9 eV for squares; 2.2 eV for circles. The volume fraction is the summation of the metastable and the stable crystalline phases for squares; only for the stable phase for circles.

5.3 CoZr₂

It is known that, on the crystallization of amorphous $CoZr_2$, the amorphous phase transforms into the stable tetragonal phase through a metastable cubic phase which has higher resistance than the tetragonal phase. We have found that there exists another intermediate crystalline phase, which has an even higher resistivity than the cubic phase, between the cubic and the stable tetragonal phase. No evidence for this phase could be found in the differential scanning calorimetry measurements nor by x-ray diffraction of samples quenched at various temperatures in the differential scanning calorimeter.

Together with Ni-Zr, Co-Zr alloys are known to form an excellent system for systematic examinations of physical properties over a wide range of compositions [1,26,99,119]. Amorphous CoZr₂ crystallizes polymorphically [80].

Altounian *et al.* [102,120] have studied the crystallization process of amorphous $CoZr_2$ by means of a differential scanning calorimetry. Structural studies were also done by using x-ray diffraction on quenched samples at each stage of crystallization as detected from the differential scanning calorimeter or by changes in electrical resistance. Their work indicates the resistance increase is associated with the formation of cubic $CoZr_2$ in which the resistivity is intrinsically high. Another study related to the nucleation and growth of the crystallization of this system have been done by Köster *et al.* [47,48] using electron microscopy. The crystallization process

seems to be well understood from those studies.

One of the advantages of our experimental method is the ability to see the transformation in real time. Here is an example of finding a new phase involved in the transformations. We sit down in front of the oscilloscope or the computer monitor both of which are connected to tue position sensitive detector controller and watch how the transformations occurs with time. With rapidly heating of the sample, the amorphous phase suddenly transforms into the cubic structure and surprisingly another intermediate phase develops before it transforms into a final structure. No analysis is needed to determine the existence of this new phase. A three dimensional plot in Fig. 5.32 shows how the phases change with time. The structures in the figure are initially the cubic phase and finally the tetragonal phase.

To see how the volume fraction of each phase changes with time, a model which is similar to Eq. 5.3 is used to fit the data. That is

$$I(q,t) = f_1(t)I_1(q) + f_2(t)I_2(q) + f_3(t)I_3(q) + f_4(t)I_4(q)$$
(5.7)

where $I_1(q)$, $I_2(q)$, $I_3(q)$ and $I_4(q)$ are the intensities of the cubic, the new metastable, the tetragonal and the amorphous phases respectively each with the corresponding fractions of $f_1(t)$, $f_2(t)$, $f_3(t)$ and $f_4(t)$. Referring to result of the fit shown in Fig. 5.33, the prefactor $f_4(t)$ is zero, because at this anneal temperature (T=720 K), the amorphous phase transforms into the cubic phase in less than the 0.1 s. One sampling time for this run was the 0.1 s. Therefore the time resolution chosen to measure the transformation was not sufficient for the amorphous to the cubic transition. This study focuses on the existence of this new phase and the transformation behaviors of three crystalline phases. Since each phase appears one by one, the diffraction patterns in Eq. 5.7 can be fit by one parameter as in Eq. 5.2. Fig. 5.33 shows the volume fraction of each phase as a function of time. The cubic phase fully transforms into the intermediate phase in nearly 8 s. The final phase appears in thereafter and the volume fraction of this phase keeps on increasing until the metastable phase has vanished.

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To see the possibility of observing the new phase by differential scanning calorimetry and conventional x-ray diffraction, some experiments were performed. As shown by the differential scanning calorimetry traces in Fig. 5.34, where the heating rate is 10 K/min, there are two peaks: one is for the exothermic heat of the cubic phase and the other is for that of the tetragonal phase. For the study of the existence of a new metastable phase, the samples were quenched at different temperatures as shown in Fig. 5.34. The x-ray experiments were then undertaken to get the complete scattering pattern.

Fig. 5.35 and Fig. 5.36 shows the scattering patterns at the different quenching temperatures. We see one figure with the cubic phase, one with the tetragonal phase and one with a mixture of these two phases. None of them shows the new intermediate phase shown in Fig. 5.37, taken from a sample which was rapidly cooled

during the *in situ* time resolved x-ray experiments.

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The question arises as to the reason why the new phase occurs in one experimental method and not in the other way. Considering the experimental methods. the main difference which can affect the existence or non-existence of the new phase is the heating and cooling rates used to quench the samples. The reason for quenching the sample is to be able to examine the sample at room temperature with x-rays, the faster the reaction rate, the higher the cooling rate that is required. Otherwise, the reaction might be completed during the cooling. The cooling rate in our time resolved experiments is nearly 10^3 K/s. By cooling the sample with this cooling rate, the same x-ray diffraction pattern at room temperature was obtained as at high temperatures (the x-ray diffraction pattern of new metastable phase for rapidly quenched sample is shown in Fig. 5.37 and the diffraction patterns of the in situ sample is shown in Fig. 5.32). Observation of the intermediate phase at room temperature implies the cooling rate was high enough to prevent further reaction in this system. Meanwhile, the cooling rate in differential scanning calorimetry is 5.3 K/s. This low cooling rate is probably not enough to freeze the state without further reaction during the cooling. Another possibility is that the heating rate is not sufficient to reach a temperature above which the new phase could appear before the temperature to the tetragonal phase has stabled.

We tried several models to determine the structure of this phase and have ruled out most cubic, hexagonal and tetragonal structures. Some of the peaks which are attributed to the new metastable are shown by the vertical lines in Fig. 5.37.

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Fig. 5.38 shows temperature and resistance as a function of time for the crystallization of amorphous CoZr_2 . In this run, the sampling time was 0.1 s. At this temperature amorphous CoZr_2 transforms into the cubic crystalline phase within 0.1 s, so the initial value of resistance is that of the cubic phase. It increases until t=0.8 s and decreases thereafter, finally approaching the resistance of the tetragonal phase. To understand the characteristics of the high resistance of the new metastable phase, whether it is caused by small particle or as an intrinsic property, requires further study.

In summary, we have discovered a new metastable crystalline phase during the crystallization of amorphous $CoZr_2$. The resistivity of this new phase is higher than that of the cubic and the tetragonal phases. A high cooling rate is required to quench this metastable phase to room temperature.

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Figure 5.32: Three dimensional plot of *in situ* x-ray scattering patterns during the crystallization of amorphous CoZr₂ at T=720 K. Initial scattering pattern is for the cubic and the final scattering pattern is for the tetragonal structures. Middle stage is the one for the new metastable structure. The x, y, z axes are the time, the wave number, and the scattering intensities. Run time is 40 s and the detector range is from q=2.36 Å⁻¹ to q=3.0 Å⁻¹.



Figure 5.33: The time dependence of volume fraction during the crystallization of amorphous CoZr_2 . The dotted, the dashed, the solid lines show the change of fraction with time for the cubic, the new metastable and the tetragonal phases. To get the volume fractions, Eq. 5.7 is used.



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Figure 5.34: Differential scanning calorimetry trace observed during the crystallization of amorphous CoZr_2 obtained with a heating rate of 10 K/min. The transverse bars labelled with the temperature in brackets represents the points where samples were quenched.



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Figure 5.35: X-ray diffraction patterns of the cubic and the tetragonal phases for $CoZr_2$. The samples were quenched in the differential scanning calorimeter. The quenched temperatures are 770 K and 850 K as shown in Fig. 5.34. The indices are (*hkl*) for each phase.



F.gure 5.36: Measured x-ray diffraction patterns of the CoZr_2 samples quenched in differential scanning calorimeter. The quenching temperatures are 720 K, 790 K and 805 K from the top as shown in Fig. 5.34. The scattering pattern on the top represents the partially crystallized cubic phase in the amorphous phase. The middle one represents the contribution of the cubic phase and the bottom one represents the contribution of the mixture of the cubic and the tetragonal phases.

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Figure 5.37: X-ray diffraction pattern of quenched CoZr_2 sample with a high cooling rate. The sample was quenched during the *in situ* time resolved x-ray experiments. The peaks with the vertical lines labelled by their wavevectors are the contribution of the new metastable phase. The other small peaks are the contribution from a small amount of the cubic and tetragonal structures.



Figure 5.38: The time dependence of temperature, resistance and power during the crystallization of amorphous $CoZr_2$.

5.4 \mathbf{FeZr}_2

It is known that, on crystallization of amorphous FeZr_2 , the amorphous phase transforms into a metastable cubic phase [26,120] which has high resistivity. The cubic phase then transforms into the stable tetragonal phase [103,121]. Our study of this system has focussed on the transformation from the amorphous to the cubic phase. One reason for interest in this transformation with time is the existence of coarsening with time in the cubic phase.

Previously, the crystallization of $NiZr_2$ and $CoZr_2$ glasses have been studied. In this section, a similar study on FeZr₂ is presented. As with $NiZr_2$ and $CoZr_2$, it is known that amorphous FeZr₂ crystallizes polymorphically. In this simple transformation from the amorphous to the cubic phase, the change of particle size will be studied in detail.

A three dimensional plot of scattering patterns as a function of scattering angle and time on the crystallization of amorphous $FeZr_2$ is shown in Fig. 5.39. The phases in the figure are initially the amorphous and then the cubic. The Miller indices of each crystalline peak are (115), (044) and (135) from lower to higher scattering angle. The time per diffraction pattern is 0.2 s for the first part and 2 s for the last part of the run. The non-existence of scattering patterns in the middle stage represents the time to transfer the first set of data to the computer and start the second. During this time the sample was held at constant temperature. The three dimensional plot shows how the peak shapes change with time. An initially broad crystalline diffraction pattern becomes narrower with time.

To get the volume fractions of each phase, a model which is similar to Eq. 5.2 is used to fit the data. That is

$$I(q,t) = (1 - X(t))I_1(q) + X(t)I_2(q,w)$$
(5.8)

where X(t) is transformed volume fraction and $I_1(q)$ is the initially measured amorphous pattern. $I_2(q, w)$, with peak width w, is the diffraction pattern for the cubic FeZr₂. In Eq. 5.2, for NiZr₂, $I_2(q)$ was the finally measured crystalline pattern. But $I_2(q, w)$ for FeZr₂ needs to be more sophisticated, since the peak width changes during the transformation. The diffraction patterns of the phase mixture in the middle stages of the transformation is not expected to be a linear combination of the initially measured amorphous pattern and the finally measured crystalline pattern. Therefore, we need another model to fit the diffraction patterns. The way we modelled the diffraction patterns of the cubic phase is as follows. We have the diffraction pattern of the cubic phase measured by x-rays, therefore we know the peak positions and the relative intensities of the peaks in the cubic phase. Using this information we can use a Gaussian functional form for each peak. Diffraction patterns are now a linear combination of two patterns and the crystalline pattern has as a parameter a common width for all peaks. Using Eq. 5.8, gives a two parameter fit for the volume fraction and the peak width.

The scattering patterns with the results of fits are represented in Fig. 5.40.

Clearly the scattering patterns evolve with time and the peaks become narrower. After 15 s, as can be seen in Fig. 5.41, there is only the crystalline cubic phase, since X(t)=1. The width of the scattering peak of the crystalline phase is all that evolves thereafter. The scattering peak width of the cubic phase (half width at half maximum) is shown in Fig. 5.42. In this figure the time axis has a logarithmic scale and the width as a function of time shows a straight line. The peak width represents the crystalline particle size in the sample by using relationship of Eq. 4.5, the change of particle size with time is shown in Fig. 5.43. In this figure, the y axis has a (size)⁵ scale and data gives a straight line, showing the growth of the particle size is $\sim t^{0.2}$. Another interesting aspect is seen in the resistance measurements. As we can see in Fig 5.44, the resistance of the cubic phase, which is higher than that of the amorphous phase, does not change when particle size grows, indicating that a high resistivity is apparently intrinsic to the cubic phase. This is in good agreement with Altounian et al. [119]. The authors also independently showed that the transformation from amorphous to cubic $FeZr_2$ is characterized by the evolution of a large number of small crystallites (30 Å size at initial times grow into micron size by annealing at 900 K for 2 h), using the transmission electron microscope and the differential scanning calorimeter [103].

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The quantitative explanations of why the domains grow with a small power law is not clear. Not many theoretical explanations or experimental studies on this growth behavior have been reported. To see the microscopic view of this growth mechanism, some other experimental method such as electron microscopy might have to be combined with more detailed time resolved studies. The process of pinning of domains walls could be observed with this method, possibly explaining the retardation of the growth at late stages of transformation. It is unusual that a low value of the growth law is observed and much work remains to be done in this system.

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Figure 5.39: Three dimensional plot of *in situ* x-ray scattering patterns during the crystallization of amorphous FeZr₂ at T=690 K. Initial scattering pattern is for the amorphous phase and the final scattering pattern is for the cubic phase. The x, y, z axes are the time, the wave number and the scattering intensities, respectively. Overall run time is 545 s. Run time of first part is 40 s, second part where the first patterns were transferred to the computer is 105 s and third part is 400 s.



Figure 5.40: Scattering patterns during the crystallization of amorphous $FeZr_2$ for a represented time sequence. The indices are (hkl) for the cubic structure. The symbols are experimental data and the lines through them are the fit with Eq. 5.8.



Figure 5.41: The time dependence of the volume crystal fraction during the crystallization of amorphous FeZr₂. The x axis ; in logarithmic scale to emphasize the volume fractions at early times.



Figure 5.42: The time dependence of peak width (half width at half maximum) during the crystallization of amorphous FeZr₂. Time is in logarithmic scale and y axis is Δq .



Figure 5.43: Change of particle size as a function of time. A straight line implies that the coarsening occurs with particle size $\sim \text{time}^{0.2}$.



Figure 5.44: The time dependence of temperature and resistance during the crystallization of amorphous FeZr₂.

5.5 Ni_{36.5}Zr_{63.5}

The simultaneous crystallization into two crystalline phases is referred to as eutectic crystallization [48]. During eutectic crystallization, the product phases can be two stable crystalline phases. Also eutectic crystallization can be followed by the primary crystallization or can be accompanied by the appearance of possible metastable phases. No composition changes are expected in the parent phase during this reaction. As can be seen in the Ni-Zr phase diagram (Fig. 5.1), crystallization of amorphous Ni_{36 5}Zr_{63 5} can be eutectic with the expected final product the two stable crystalline phases of NiZr and NiZr₂ [3,106]. Result of time resolved x-ray measurements again show something which was not expected.

The interesting aspect of studies of crystallization behavior of this composition is the existence of a new phase along with the known crystalline phases of NiZr and NiZr₂. Fig. 5.45 represents the time evolution of scattering patterns during the crystallization. The times shown correspond to transformed volume fraction X=0, 0.1, 0.25, 0.4 and 1. Lines through the data in the figure are fits to the diffraction patterns with the assumption of a linear decomposition of each scattering pattern into four separate parts: an amorphous pattern $I_1(q)$, a crystalline NiZr₂ pattern $I_2(q)$, crystalline NiZr pattern $I_3(q)$ and an extra pattern $I_4(q)$. The model used is

$$I(q,t) = (1 - X(t))I_1(q) + X(t)(f_2(t)I_2(q) + f_3(t)I_3(q) + f_4(t)I_4(q))$$
(5.9)

where X(t) is total volume fraction transformed. The prefactors $f_2(t)$, $f_3(t)$ and

 $f_4(t)$ are the contributions of crystalline NiZr₂, crystalline NiZr and extra phases, respectively. The amorphous pattern $I_1(q)$ is the initially measured pattern. The crystalline patterns, $I_2(q)$ and $I_3(q)$, are independently measured x-ray diffraction patterns for crystalline N_1Zr_2 and crystalline NiZr samples. The application of the independently measured x-ray diffraction patterns for model 5.9 and the determination of the extra line shape is as follows. We have the peak positions and relative intensities of the two expected phases from the independently measured x-ray diffraction patterns. For the last scattering pattern of the run, where the amorphous phase has fully disappeared, it might be expected that the diffraction pattern is a summation of the diffraction from the tetragonal $NiZr_2$ and orthorhombic N_1Zr . We found that the diffraction pattern is not just the summation of the expected two patterns. We must introduce another line to fit the data. This extra line shape is required to fit all the diffraction patterns through out the run. The line we have determined is shown in Fig. 5.45 as a solid line. Fig. 5.46 represents a blow-up of the scattering pattern for the final time. The solid line through the data is a fit to the scattering pattern with the summation of the three parts without any amorphous contribution. Clearly, by inserting an extra scattering pattern, the fit is reasonable The contribution of the new phase remains even after the amorphous phase has fully disappeared in this experiment Also we found the prefactors $f_2(t)$ and $f_3(t)$ were constant in time. Therefore the diffraction model in Eq. 5.9, once these constants are determined, has two parameters, the transformed volume fraction X(t) and the

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prefactor $f_4(t)$.

The results of this fit is shown in Fig. 5.47. This figure shows the relative volume fractions of each phase with time. The volume fractions of each phase can not be determined at this stage of analysis because the diffraction profile of the new phase is not fully determined. In this figure, $f_2(t)$ and $f_3(t)$ are constant, 0.8 and 0.19 respectively. But $f_4(t)$ changes with time. It increases initially and then stays nearly constant, indicating that the rate of transformation for the three phases is not simultaneous. One thing we can say, by only considering the crystallization behavior of the NiZr₂ and NiZr compositions, is that the crystallization mode of this composition is eutectic. The relative fractions of those two crystalline parts are constant with time, indicating the simultaneous crystallization of the two phases. We have not performed high temperature or long time experiments for this system. Therefore we have not much data on the transformation of this extra phase, when or if it disappears and nor on its relationship with the expected phases.

The question is 'what is this extra phase?'. Altounian *et al.* [103] studied the crystallization of amorphous $Ni_{42}Zr_{58}$ and reported the existence of the new metastable phase (also refer to Ref. [3,102]). By using differential scanning calorimetry, x-ray diffraction and electron microscopy, the authors determined the structure of the metastable phase as a cubic phase. The behaviors of the new phase on the crystallization of $Ni_{36.5}Zr_{63.5}$ in our experiments are similar in several ways to the one found by these above authors. First of all, the position of one of the largest scattering peaks from these authors is the same as that shown in Fig. 5.47. Secondly, the resistance initially increases with the appearance of the new phase and decreases thereafter with phase separation into the crustalline NiZr and NiZr₂ phases (Fig. 5.48). Thirdly, the reaction rate of the new phase is faster than that of the stable crystalline phases. So, independently measured results by using different methods both show the appearance of this new phase.

In summary, there exist a new phase during the crystallization of amorphous $Ni_{36.5}Zr_{63.5}$. Although the prefactors $f_2(t)$ and $f_3(t)$ in Eq. 5.9 remain constant, suggesting simultaneous phase separation, the prefactor of the new phase changes with time during the crystallization. To understand the crystallization kinetics of this composition and the properties of the new phase, possibly a crystalline cubic phase, more studies such as real time x-ray diffraction experiments at higher temperature or electron microscopy will be required.



Figure 5.45: Diffraction patterns for a representative time sequence during the crystallization of amorphous $Ni_{365}Zr_{635}$ at T=690 K. Symbols represent the measured x-ray scattering and the solid line through them are the results of a fit with Eq. 5.9. The amorphous contribution is dashed, the known crystalline contribution is dotted (summation of contribution of crystalline NiZr₂ and crystalline NiZr) and the new phase contribution is solid. The time per diffraction pattern is 0.5 s.

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Figure 5.46: Diffraction pattern for a final time during the crystallization of amorphous Ni_{36 5}Zr_{63 5}. Symbols represent measured x-ray scattering pattern and the solid line through them is the result of the fit with Eq. 5.9. The N₁Zr₂ contribution is dashed, the NiZr contribution is dotted with the indices (hkl) and new phase contribution is solid.



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Figure 5.47: The time dependence of relative volume fraction during the crystallization of amorphous Ni_{36 5}Zr_{63.5}. The circle is X(t), the square is $X(t) \times f_2(t)$, the dashed is $X(t) \times f_3(t)$, the dotted is prefactor $f_4(t)$ and the line is $X(t) \times f_4(t)$ in the Eq. 5.9. the prefactors $f_2(t)$ and $f_3(t)$ are 0.8 and 0.19, respectively.



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Figure 5.48: The time dependence of temperature, resistance and power during the crystallization of amorphous $Ni_{36.5}Zr_{63.5}$ at T=690 K.

Chapter 6

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Conclusions

We have presented a new experimental method for the study of phase transformations and applied this method to the study of crystallization kinetics of zirconium based metallic glasses. By using *in situ* time resolved experimental method, we have overcome many of the experimental barriers which conventional methods face. Our results of the time resolved x-ray measurements have shown many unexpected phenomena and have enabled us to solve many problems. These results indicate how it is exciting and important to study phase transformation *in situ*. But as we have seen in this thesis, as many problems remain unsolved as many have been solved. Specifically, the appearance of the new phases during many of the crystallizations complicated matters and theoretical studies, as well as further experimental studies, are required to understand each transformation process. The study of phase transformations with *in situ* time resolved x-ray measurement is just in its infancy. We have opened a new area of experimental methods for the study of phase transformations. We expect many experiments can be performed on many systems and many problems will be solved by this new method.

The two parts of this thesis, the development of *in situ* time resolved x-ray experimental methods and the application of this new method to crystallization kinetics, can be summarized as follows.

1. The main conclusion of the development of the new experimental method are as follows.

(1.1) By resistively heating the sample in helium atmosphere, we get heating rates of over 10^4 K/s and cooling rates of 10^3 K/s.

(1.2) By using a position sensitive detector and a special monochromator, we can acquire diffraction patterns as fast as every 3 ms.

(1.3) By using an infrared pyrometer, we can read and control the sample temperature, overcoming the difficulties of reading temperature by using a thermocouple.

(1.4) By using synchrotron radiation, we get the high diffraction intensity which is crucial for the structural measurements of the fast reactions.

(1.5) In sutu time resolved x-ray experimental method enables us to study fast reactions.

(1.6) We have demonstrated many different aspects of structure that can be measured as a function of time. An ability to follow the evolution of diffraction patterns in real time enables one to qualitatively investigate the transformation kinetics. Specifically, there is the possibility to discover new phases. A quantitative measurements of intensities for the different components of diffraction pattern allow us to get volume fractions of each of the phases. We can measure the positions of the Bragg peaks and therefore lattice constants as a function of time. Any time evolution of the width of these peaks enable us to measure the time dependence of the microstructure.

2. The main conclusion of the study of the crystallization kinetics of the amorphous NiZr₂, CoZr₂, FeZr₂ and Ni_{36 5}Zr_{63 5}, using *in situ* time resolved experimental methods, can be summarized as follows.

(2.1) NiZr₂

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Conventional Crystallization:

Isothermal crystallization behavior follows closely the expected dependencies from earlier works. A simultaneous measurement of the x-ray diffraction patterns, temperature, power and resistance of a sample in real time demonstrates the advantage of the new experimental method. Detailed structural investigation shows that the amorphous phase transforms into the stable crystalline phase with a small amount of an intermediate phase. In spite of a small amount of this phase present, a model based only on the coexistence of amorphous and stable phases fits the data Transient nucleation theory, with constant growth rate, is applied. This simple model fits our results well, explaining how kinetics of crystallization occur, *i.e.* by nucleation and growth. Resistance decreases from high values in the amorphous phase to low values in the crystalline phase.

Rapid Crystallization:

Structural investigation shows that there is a new metastable crystalline phase. The existence of the metastable phase which evolves into a stable phase has been examined in different ways. The pixel intensity at q=2.55 Å⁻¹ shows the transformation does not occur in simple manner. Instead of simply increasing or decreasing, this pixel intensity increases and then decreases because of the presence of the metastable phase. The resistance change also shows that the phase transformation does not occur in simple manner. The resistance increases with the appearance of metastable crystalline phase and then decreases. This increase is explained by the resistance of metastable phase being higher than that of the amorphous phase. The reaction kinetics can not be determined by a unique Avrami exponent. Activation energy has been measured to be 2.2 eV for the appearance of the stable phase.

(2.2) CoZr₂

It is known that crystallization occurs through the sequence: amorphous phase \rightarrow cubic phase \rightarrow tetragonal phase. We found a new metastable phase which appears between the cubic and the tetragonal phases. The resistance of the new phase

is higher than that of the cubic and the tetragonal phases. We couldn't see any evidence for the new phase by x-ray diffraction from samples which were quenched in the differential scanning calorimeter, implying that the important information on the structural changes during the crystallization of metallic glasses may be lost if the experiment is not conducted *in situ*. The new phase discovered can be studied at room temperature if the sample is quenched by high cooling rates.

(2.3) FeZr₂

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It is known that crystallization occurs through the sequence: amorphous phase \rightarrow cubic phase \rightarrow tetragonal phase. We have focussed on the transformation from the amorphous phase to the cubic phase and found the occurrence of coarsening in cubic phase. The exponent of growth law is nearly 0.2, *i.e.* R ~ t^{0.2} with particle size R and time t.

(2.4) Ni_{36 5}Zr_{63 5}

It was expected that the crystallization of amorphous $Ni_{36.5}Zr_{63.5}$ should occur through eutectic phase separation of tetragonal NiZr₂ and orthorhombic NiZr. We found that the phase separation occurs with the appearance of another phase which appears with a higher reaction rate than that of expected phases This extra phase may be closely related to the metastable phase that Easton *et al.* [102] and Altounian *et al.* [103] have reported previously.

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