CRYSTALLIZATION KINETICS OF TWO METALLIC GLASSES BY MOSSBAUER SPECTROSCOPY

Thesis

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CRYSTALLIZATION KINETICS OF TWO METALLIC GLASSES BY MOSSBAUER SPECTROSCOPY

THESIS

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by

Denis E. Beller, B.S. Captain USAF Graduate Nuclear Engineering March 1981

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Preface

This thesis describes my efforts to determine the crystallization kinetics of two amorphous iron alloys, Fe$_{80}$B$_{20}$ and Fe$_{80}$P$_6$C$_{5.5}$B$_{10}$. The objectives of this study were: 1) to anneal the glasses at various temperatures, 2) to take Mossbauer spectra during the annealing, 3) to analyze the spectra to determine the growth of crystals, and 4) to use the crystallization rates to calculate the activation energy and projected lifetimes at 473 K. This thesis will summarize past work in this area, describe the equipment and methods, and present analysis of the Mossbauer spectra and the results, conclusions and recommendations.

I thank Dr. Harold Gegel of the Air Force Materials Laboratory for sponsoring this study and supplying the glassy metal ribbons. I especially thank my advisor, Dr. George John, for his continuous support and guidance. Finally, I am grateful to my wife, Judy, and my sons, David and Timothy, for their constant devotion and support during this long study.
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Abstract

In this study, Mossbauer spectroscopy was used to examine thermal aging of two metallic glasses. Fe$_{80}$B$_{20}$ was isothermally annealed at 573, 604, 611, and 626 K; and Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$ was annealed at 614, 716, and 744 K. The activation energy of Fe$_{80}$B$_{20}$, determined from the growth of α-Fe crystals, was 0.256 ± 0.006 MJ/mole. The projected lifetime of this glass, based on the onset of crystallization, is 400 years. No quantitative data were obtained for Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$; however, based on the higher temperature required for crystallization, it is expected to have a longer lifetime.
CRYSTALLIZATION KINETICS OF TWO METALLIC GLASSES BY MOSSBAUER SPECTROSCOPY

I. Introduction

Mossbauer spectroscopy is becoming an increasingly important tool for studying the environments of nuclei. In this study, it was used to examine the crystallization characteristics of Fe$_{80}$B$_{20}$ and Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$ amorphous alloys. These materials, commonly called metallic glasses, crystallize during accelerated aging at high temperatures.

Background

The glassy metals exhibit useful magnetic, as well as material (tensile strength, hardness, flexibility), properties. The Air Force Materials Laboratory has become interested in their possible use in magnetic devices for Air Force weapons systems. As a result of this interest, in 1978 Schmidt (Ref 1) and Roberts (Ref 2) used Mossbauer spectroscopy to study the atomic structure of a few of the glassy metals, including Fe$_{80}$B$_{20}$. Because of projected high-temperature applications, the Materials Laboratory is concerned about thermal aging of these materials. Knowledge of the glasses' expected lifetimes at operating temperatures around 473 K is needed. To predict the aging rates of these amorphous materials, one must know

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1See Appendix E for a review of possible applications.
their crystallization characteristics. Many methods have been used to determine these rates; all require measurements at 100 to 200 K above the expected operating temperature. In this study, Mossbauer spectroscopy was used to examine the growth of crystals in the metallic glasses Fe$_{80}$B$_{20}$ and Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$.

**Problem**

The problem investigated in this study was to determine the thermal aging rate of metallic glasses. Specifically, the kinetics of crystallization of Fe$_{80}$B$_{20}$ and Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$ were studied. These glasses were examined by: 1) isothermal annealing, 2) taking Mossbauer spectroscopy during annealing, 3) evaluating the spectra to determine growth of $\alpha$-Fe crystals, and 4) using the crystallization rates at various temperatures to determine the Arrhenius constant.

**Scope**

This study was limited to the investigation of only two of the glassy metals, Fe$_{80}$B$_{20}$ and Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$. The temperature ranges were respectively 573 to 626 K and 716 to 744 K. The annealing periods were from one day at the high temperatures to two weeks at the lowest temperatures. No attempt was made to determine the structure of either the amorphous or the crystalline material. In addition, the literature studied was limited to only sources available at the School of Engineering, Air Force Institute of Technology.

**Review of the Literature**

This section contains a review of some of the many studies of the metallic glasses. These studies are mainly...
concerned with three characteristics of the glasses: 1) amorphous structure, 2) temperature dependence of their magnetic properties, and 3) thermal aging (or crystallization) characteristics. Some of the results of these studies will be presented in the discussion section in Chapter IV.

Luborsky studied the crystallization of $\text{Fe}_{80}\text{B}_{20}$, $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_{6}$, and $\text{Fe}_{40}\text{Ni}_{40}\text{B}_{20}$, using magnetic methods and differential scanning calorimetry (Ref 3). Using the temperature of onset of crystallization at various heating rates, he determined the activation energy for the three materials. He also showed that thermal stability increased with the number of atomic species, i.e., that $\text{Fe}_{80}\text{B}_{20}$ was the least stable of the three glasses. Fukamichi and others studied the magnetization, electrical resistivity, thermal expansion, and differential thermal change of a variety of Fe-B glasses (Ref 4). They determined that the crystallization mechanism of the Fe-B glasses depended on the concentration of boron. Chien studied $\text{Fe}_{80}\text{B}_{20}$ from 4.2 K up to 1050 K, using Mossbauer spectroscopy, and found that it crystallized to $\alpha$-Fe and $\text{Fe}_3\text{B}$ when annealed at a high heating rate, but found only $\text{Fe}_2\text{B}$ at low heating rates (Ref 5). Luborsky and Lieberman examined the crystallization kinetics of the Fe-B glasses (12 to 28 percent boron) by differential scanning calorimetry (Ref 6). They determined that for 18 to 28 percent boron, the activation energy for the onset of crystallization was independent of boron concentration. However, Tarnoczi and others studied the role of $\text{Fe}_3\text{B}$ in the crystallization of Fe-B glasses, and concluded
that Fe$_{80}$B$_{20}$ was most stable (Ref 7). Matsuura, in a study similar to Luborsky and Lieberman's above, used differential thermal analysis on 12 to 20 percent boron Fe-B glasses (Ref 8). His results, obtained above 700 K, led to the conclusion that the formation of α-Fe accompanies the crystallization of Fe$_3$B.

Chien and others did a lengthy study on Fe-B glasses (14 to 28 percent boron) and crystalline Fe$_3$B using Mossbauer spectroscopy and magnetization measurements (Ref 9). Kemeny and others used Mossbauer spectroscopy, differential scanning calorimetry, and magnetization measurements for a thorough investigation of the structure and crystallization of Fe-B metallic glasses (12 to 25 percent boron) (Ref 10). For 16 to 25 percent boron, they concluded that crystallization proceeds by the formation of α-Fe and Fe$_3$B in an eutectic process. They also deduced that the glass structure should be based on locally distorted, quasi-crystalline Fe$_3$B.

Schaafsma and others have also done a lengthy crystallization study on two Fe$_{80}$B$_{20}$ glasses (Ref 11). They concluded that the crystallization mechanism did not change between 580 and 640 K. They also found that nucleation did not control the crystallization rate; i.e., that crystal nuclei exist in the as-quenched amorphous material. Finally, Kopcewicz used Mossbauer spectroscopy to study radio-frequency annealing of Fe$_{40}$Ni$_{40}$B$_{20}$ (Ref 12). He found that as a result of pyroelectrically induced atomic vibrations, a strong radio-frequency field caused crystallization in LN$_2$-cooled samples.
Assumptions

The following were assumed to be true at the outset:

1) The Fe$_{80}$B$_{20}$ and Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$ alloys were amorphous.

2) During annealing α-Fe and metastable Fe$_3$B were formed.

3) The compositions were true to within one percent.

Overview

The theory of the Mossbauer effect has been well documented and will not be presented here; however, the use of Mossbauer spectroscopy to study nuclear environments is presented in Chapter II, along with the theory of crystallization of Fe-B glasses. The Mossbauer equipment, annealing system, experimental procedures, and data processing are described in Chapter III. Chapter IV contains the results and discussion, and Chapter V contains the conclusions and recommendations.
II. Theory

The theory of the Mossbauer effect has been fully developed and is well understood (see, e.g., Ref 13 and 14). For a condensed and simplified explanation, see Roberts' thesis (Ref. 2: 3-11). Mossbauer spectroscopy measures the hyperfine fields of nuclei. This is possible because the hyperfine field interacts with the nuclear dipole moment, which, for iron-57, splits the resonant-absorption energy into six energy levels. The magnitudes of these energies are directly proportional to the value of the hyperfine field, which is characteristic of the electron environment of the nucleus. Thus, for nuclei in a crystal, there are different six-peak spectra (with Lorentzian line shapes) for each magnetically inequivalent site. For an amorphous material which has only short-range order, there are very few magnetically equivalent sites. The glass spectrum, then, is a combination of many different six-peak spectra, with a probability distribution $P(H)$ describing the nuclear hyperfine fields. The $P(H)$ of Fe$_{80}$B$_{20}$ have been described by Schmidt (Ref 1) and Vincze (Ref 15) as a binomial distribution. This distribution was related to the number of nearest neighbors of iron and non-iron nuclei. However, others have shown that the glass spectra can be described by a model-independent probability distribution (Refs 15, 16, and 17). Schurer and
and Morrish have shown that a single six-line pattern, using Gaussian line shapes, describes the glass spectrum reasonably well (Ref 16: 619). This method is used in this study for the Fe$_{80}$B$_{20}$ glass.

When a metastable metallic glass is heated, it undergoes atomic rearrangement to a more stable, but still amorphous, state (Ref 18: 577). With further heating, it begins to crystallize. This crystallization has been described as a diffusion process, as one or more species migrates out of the amorphous region (Ref 11: 4428). For the Fe-B glasses, the possible crystalline states are α-Fe, FeB, Fe$_2$B, and Fe$_3$B. Fe$_2$B is expected to form during crystallization of the amorphous phase because it is much more stable than Fe$_3$B. For Fe$_{80}$B$_{20}$, however, the metastable Fe$_3$B (or Fe$_{75}$B$_{25}$) is much nearer the original composition than Fe$_2$B (or Fe$_{67}$B$_{33}$). Thus, others have found that α-Fe and Fe$_3$B are the species formed during annealing of Fe$_{80}$B$_{20}$ (Refs 7: 1026; 8: 232; 10: 485; 11: 4429). While some determined that iron diffused from the glass to form α-Fe, leaving amorphous Fe$_{75}$B$_{25}$, which subsequently crystallized to Fe$_3$B (Ref 11: 4429), others deduced that Fe$_3$B crystallized accompanied by the simultaneous formation of α-Fe (Ref 8: 233). For a glass with many species, such as Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$, there are many possible crystalline states. These include FeB, Fe$_2$B, Fe$_3$B, Fe$_3$C, Fe$_5$C, and combinations of these by atomic substitution, along with Fe.

The isothermal crystallization of an iron-based glass can be followed, then, by examining the growth of the six-peak
α-Fe spectrum in a series of Mössbauer spectra. The crystalline fraction $x(t)$ is the ratio of the volume of α-Fe crystals formed at time $t$ to the volume in the fully crystallized sample. It can be described by the Johnson-Mehl-Avrami equation (Ref 11: 4426):

$$x(t) = 1 - \exp \left[-(k(T)t)^n\right]$$  \hspace{1cm} (1)

When rearranged, Eq (1) becomes

$$\ln \ln \frac{1}{1-x(t)} = n \ln k(T) + n \ln t$$  \hspace{1cm} (2)

which yields a straight line plot with slope $n$. Above, $k(T)$ is a temperature dependent constant, and the exponent $n$ is determined by the nucleation and growth characteristics of the crystallization. The time $t_x(T)$ to crystallized fraction $x$ can be determined from Eq (2) for a series of isothermal measurements. Then, for a thermally-activated diffusion process, the Arrhenius equation describes the lifetime $t_x$ at constant $x$ as a function of temperature $T$:

$$t_x = k_0^{-1} \exp \left(\frac{E_A}{k_BT}\right)$$  \hspace{1cm} (3)

where $k_0$ is a frequency factor, $k_B$ is the Boltzman constant, and $E_A$ is the activation energy of the crystallization process expressed as energy per atom (or per mole) (Ref 11: 4427). Eq (3), when rearranged, also yields a straight line plot with slope $E_A/k_B$:

$$\ln t_x = \ln k_0^{-1} + (E_A/k_B)T^{-1}$$  \hspace{1cm} (4)
The above kinetic parameters can be derived from relatively quick measurements at high temperatures. If the assumption is valid that the crystallization process is the same over a large range of temperatures, then these constants can be used to predict the crystallization rate at lower temperatures. In this study, the crystallized fractions $x(t)$ were determined from the amplitudes of the $\alpha$-Fe portions of Mossbauer spectra. The half lives $t_{\text{50}}$ were then determined by least-squares curve fitting, and were used to determine the activation energy from the Arrhenius plot.
III. Equipment and Procedures

In this section the Mossbauer spectroscopy equipment and annealing system are described. The procedures for preparing the glass samples and assembling them in the heater are included. Annealing the samples, taking the Mossbauer spectra during annealing, and analyzing the spectra are also described.

Mossbauer Equipment

The major Mossbauer spectroscopy components included a constant-acceleration velocity transducer (motor), a linear amplifier/single channel analyzer, a krypton-filled proportional counter, and a Mossbauer control unit (MCU). All were manufactured by Ranger Electronics. The Mossbauer spectrum was taken on an RIDL 400 multichannel analyzer (MCA), operated in the time-sequential scaling mode. With the exception of the time-base oscillator, which was an RIDL model 54-6, the equipment is the same as that described by Skluzacek (Ref 19: 5-11), Schmidt (Ref 1: 11-15), and Roberts (Ref 2: 12). The source, connected directly to the motor, was approximately 6 mCi cobalt-57 in a rhodium foil.

Annealing System

The annealing system consisted of a heater, a thermocouple reader, a vacuum system, and one of two temperature controllers. Ranger Engineering built the heater (Fig 1) as
a prototype. The heating elements were two graphite discs (0.135 ± 0.002 mm x 25.4 mm). The sample was held between the heating discs and aligned with two aluminum foil windows (0.025 ± 0.001 mm x 25.4 mm). There were two iron-constantan thermocouples inside the heater; one was located in a slot at the edge of the heating element frame, the other was centered on the sample. The Omega thermocouple reader was calibrated with ice, boiling water, and molten tin. The vacuum system consisted of a forepump and an oil diffusion pump topped with liquid nitrogen. Its purpose was to prevent convective heat transfer to the heater body. The first temperature controller,
a Lambda regulated DC power supply, was designed to provide manually-set constant current. Because of the failure of this power source, it was replaced with a Gardsman temperature controller, which was connected through a filament transformer to the heater. It supplied AC power, which produced an alternating field between the heating elements. This produced a problem which is discussed in Chapter IV. The edge thermometer supplied feedback to the controller. Neither controller regulated the temperature adequately; temperatures varied ±2 K throughout the runs, with occasional drops (less than 1% of annealing time) of up to 10 K.

A sketch of the source-absorber-detector system is shown in Fig 2. The distance from the source to detector window was approximately 10 cm.
Sample Preparation

Dr. Harold Gegel, of the Air Force Materials Laboratory, provided the glassy metal ribbons which were used to prepare the samples. Battelle Laboratories at Columbus, Ohio, manufactured the ribbons by spin-cooling the molten alloy on a cooled rotating drum. The Fe_{80}B_{20} (nominal atom percent) glass ribbons were 28.8 ± 0.5 μm thick, the Fe_{80}P_{6.5}C_{3.5}B_{10} ribbons were 27.9 ± 0.5 μm thick, and the width of both varied from 0.5 to 1.2 mm with an average width of about 0.8 mm. The samples were prepared as a parallel array of the ribbons in 32 ± 2 mm long strips, to form an absorber 25 mm wide. The strips were held parallel with cellophane tape at the top and bottom and then bonded at one end with cyanoacrylate cement to a boron nitride disc (25.4 mm diameter). This was done to prevent thermal stresses which have been observed to affect the spectra (Ref 20). When the cement had dried, the glass strips were trimmed to the dimension of the boron nitride disc. Since the cement degraded during the annealing, the strips were held unfettered and remained free of thermal stress.

Heater Assembly

The sample and heating discs were assembled into the heater as shown in Fig 3. One graphite disc was inserted into the ceramic frame, followed by a clean boron nitride disc. The fine thermocouple was then centered on the boron nitride disc. The second boron nitride disc, with the glass couple attached, was then inserted, followed by the second graphite disc. The assembly was secured by two small plates and screws.
The heater assembly was then inserted into the heater body, secured, and vacuum was applied.

**Annealing and Data Collection**

Once the heater was assembled and degassed overnight, the isothermal annealing run began. The heating rate was 5 to 15 K/min up to 473 K, and held there until again degassed. When the vacuum dropped below $10^{-3}$ Pa, the temperature was increased to the desired annealing point. Generally, this took about five minutes. The initial Mössbauer spectrum started as soon as this temperature was reached. Additional spectra were then taken in sequence until the sample was near full
crystallization. The time between the end of one spectrum and the beginning of the next was about ten minutes, which was the time necessary to punch the 400 channels of data onto paper tape. The isothermal annealing runs lasted from 10.5 hrs for Fe$_{80}$B$_{20}$ at 626 K, up to 315 hrs for Fe$_{80}$B$_{20}$ at 573 K. To fully crystallize the samples, the temperature was increased for about 18 hrs following each annealing run (to 640 K for Fe$_{80}$B$_{20}$, 750 K for Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$). The temperature was then lowered to the original annealing point, and a final Mossbauer spectrum was taken. The spectrum collection periods were between 1 and 24 hrs, depending upon the crystallization rate of the sample.

Data Processing

The Mossbauer spectra were analyzed by a least-squares minimization curve fitting program developed at the Argonne National Laboratory. This program, GENFIT, has been modified by Skluzacek (Ref 1: 21), Schmidt (Ref 1: 21-22), and Roberts (Ref 2: 18). It is listed as Appendix A of Roberts' thesis (Ref 2: 50-60), and will not be repeated here. A user-supplied subroutine, CALFUN, provides the mathematical model to be fitted, along with the desired variable parameters. Three different CALFUNs were used for this study. They are explained below.

Subroutine CALFUN (Gaussian fit to Fe$_{80}$B$_{20}$ class). This subroutine fits Gaussian line shapes to the Fe$_{80}$B$_{20}$ spectra taken at the beginning of each annealing run.though
that can lead to erroneous values of the average hyperfine field (Ref 10: 478), it did provide reasonable fits. Its purpose was to provide the glass spectra to be included in the CALFUn below. The variables which were included in this subroutine were:

1. Baseline: the average counts in the background of the Mossbauer spectrum.
2. Magnetic field: one value of average hyperfine field, in kOe (100 kOe = 7.96 MA/m).
3. Isomer shift: one value of average isomer shift for the glass, in mm/sec.
4. Quadrupole split: one value of average quadrupole split for the glass, in mm/sec.
5. Total intensity: one value for total intensity (average) of peaks one and six, expressed as a fraction.
6. Relative intensity: one value of the ratio of the average intensity of peaks two and five to the average intensity of peaks one and six.
7. Linewidths: six values of the full width at half maximum intensity (FWHM); one for each of the six Gaussian line shapes, in mm/sec.

The areal ratios of peaks three and four were constrained to one-third the area of peak one. This subroutine is listed as Appendix A. It was called GAUSSCALF.

Subroutine CALFUn [Crystallized Fe$_{80}$B$_{20}$]. This subroutine provides for fitting the data with one six-peak α-Fe
(Gaussian) glass spectrum. The variable parameters are:

1. Baseline: as in GAUSSCALF above.
2. Magnetic fields: one hyperfine field for α-Fe and one each for three Fe$_3$B sites, in kOe.
3. Isomer shifts: one each for α-Fe and the three Fe$_3$B sites, in mm/sec.
4. Linewidths: one value of FWHM for peaks one and six, one for peaks two and five, and one for peaks three and four, of all three Fe$_3$B sites, in mm/sec.
5. Total intensities: one value of total intensity for each of α-Fe, Fe$_3$B, and the glass.

To simplify—and reduce the time and cost of—processing, this subroutine required many constraints. The glass spectrum was constrained to those parameters found in GAUSSCALF above, only its intensity was variable. The linewidth of α-Fe was constrained to that value found for the fully crystallized spectrum, and all six peaks used this same value. The areal ratios were 3:2:1:1:2:3 for peaks 1:2:3:4:5:6 of α-Fe and Fe$_3$B. The relative intensities of the three Fe$_3$B sites were 1:1:1, and their linewidths were constrained to be equal for similar peaks. Finally, the quadrupole splits of α-Fe and the three Fe$_3$B sites were constrained to zero. This subroutine, called $11\textsc{C}.\text{LF}$, is listed as Appendix B.

Subroutine CALFUN (for α-Fe, peaks one through six). This version of CALFUN provides for analysis of only peaks one and six of the α-Fe crystallized from the glass. It includes a
Gaussian shaped background, and does not fit the center portion of the spectrum. The required variables are:

1. Baseline: as in GAUSSCALF.
2. Magnetic fields: one value for the α-Fe hyperfine field, and one value for the background, in kOe.
3. Total intensities: one value for the total intensity of peaks one and six of α-Fe, and one value for the background.
4. Linewidths: one value of FWHM for α-Fe, and one value for the background, in mm/sec.
5. Isomer shifts: one value of isomer shift for α-Fe and one value for the background, in mm/sec.

This subroutine is listed in Appendix C, and was called ALPHA-BG. Appendix D contains instructions for using GENFIT and CALFUN, and discusses required alterations to FIVECALF for spectra taken at other temperatures.

**Goodness of Fit**

The goodness of fit to the Mossbauer spectra is measured by Chi-squared, which is generated by GENFIT. Its value is defined by:

\[
\chi^2 = \sum_{i=1}^{N} \frac{(\text{data point}_i - \text{calculated point}_i)^2}{\text{data point}_i}
\]

where \(N\) is the number of data points fitted. Theoretically, the values of Chi-squared obtained for a number of spectra should be randomly distributed around the number of data points, in the limit approaching this number.
IV. Results and Discussion

In this section, the results of the spectra analyses and crystallization rate determinations are presented. These results are compared in the discussion to those derived by others. Table 1 lists the isothermal annealing runs with the sample material, temperature, annealing period, slope of the Johnson-Mehl-Avrami plot, crystallization half-life $t_{1/2}$, and heater power (AC or DC). Figures 4 through 15 are examples of the Mossbauer spectra taken during the annealing runs. The title of each figure lists the sample material, temperature, annealed time, CALFUN used, and crystalline fraction. The crystalline fraction was calculated as the ratio of the value of the $\alpha$-Fe intensity of that run to the value of the fully crystallized state. Figures 4 (2.89 hr at 573 K) and 5 (48.9 hr at 573 K) show that the glass spectrum changes very little before crystallization. Figure 6 shows the $\alpha$-Fe peaks just after the onset of crystallization; note that the remainder of the spectrum still resembles the glass spectra. Figures 7 and 10 (19 and 100 percent crystallized) include the locations of the peaks of the $\alpha$-Fe and three $\text{Fe}_3\text{B}$ spectra, along with the values of their hyperfine fields (in $\text{MA/m}$). Note that the values of the three $\text{Fe}_3\text{B}$ fields increased with time, which was true of all isothermal annealing runs. However, the linewidths of these peaks decreased with time, as much as 50 percent. Figures 9 and 10
### TABLE I
Annealing Runs

<table>
<thead>
<tr>
<th>Run</th>
<th>Glass</th>
<th>Temperature (K ± 2 K)</th>
<th>Annealing Period (hr)</th>
<th>Half-life (hr)</th>
<th>Slope n</th>
<th>Power Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>573</td>
<td>315</td>
<td>604 ± 57</td>
<td>1.60 ± 0.22</td>
<td>DC</td>
</tr>
<tr>
<td>2</td>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>604</td>
<td>45</td>
<td>34.0 ± .5</td>
<td>1.77 ± .24</td>
<td>AC</td>
</tr>
<tr>
<td>3</td>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>611</td>
<td>76</td>
<td>18.0 ± 0.7</td>
<td>1.50 ± 0.06</td>
<td>DC</td>
</tr>
<tr>
<td>4</td>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>611*</td>
<td>48</td>
<td>21.1 ± 1.8</td>
<td>1.17 ± 0.08</td>
<td>DC</td>
</tr>
<tr>
<td>5</td>
<td>Fe$<em>{80}$B$</em>{20}$</td>
<td>626</td>
<td>10.5</td>
<td>6.69 ± 0.54</td>
<td>1.57 ± 0.14</td>
<td>DC</td>
</tr>
<tr>
<td>6</td>
<td>Fe$<em>{80}$P$</em>{6.5}$C$<em>{3.5}$B$</em>{10}$</td>
<td>614</td>
<td>27</td>
<td>No crystallization observed</td>
<td></td>
<td>AC</td>
</tr>
<tr>
<td>7</td>
<td>Fe$<em>{80}$P$</em>{6.5}$C$<em>{3.5}$B$</em>{10}$</td>
<td>716</td>
<td>48</td>
<td>&lt;2.9</td>
<td></td>
<td>AC</td>
</tr>
<tr>
<td>8</td>
<td>Fe$<em>{80}$P$</em>{6.5}$C$<em>{3.5}$B$</em>{10}$</td>
<td>744</td>
<td>25</td>
<td>&lt;0.5</td>
<td></td>
<td>AC</td>
</tr>
</tbody>
</table>

*This sample was annealed 13 days at 573 K, and was about 22% crystallized at the beginning of this run.*
Fig. 6. Mössbauer Spectrum of Fe$_{80}$B$_{20}$, 573 K, 111 hr, FIVECALF, $x = 0.0512$
Fig. 7. Mössbauer Spectrum of Fe$_{80}$B$_{20}$, 573 K, 281 Hr, FIVECALF, $x = 0.190$
Fig 9. Mossbauer Spectrum of Fe$_{80}$B$_{20}$, 611 K, Fully Crystallized, FIVECALF
Fig. 10. Mössbauer Spectrum of Fe$_3$O$_4$B$_{20}$, 611 K, Fully Crystalized
FIVECALF with Quadrupole Splitting
Fig. 11. Mössbauer Spectrum of Fe$_{80}$B$_{20}$, 611 K, Run 3, Fully Crystallized FIVECALF
Fig. 12. Mössbauer Spectrum of Fe$_{80}$B$_{20}$, 604 K, 13.8 Hr, FIVECALF, $x = 0.316$
Fig. 15. Mossbauer Spectrum of Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$, 716 K, Fully Crystallized ALPHA-BG.
clearly demonstrate the effect of constraining the last quadrupole splits to zero: Chi-squared was 508 for Fig 9, but with quadrupole splitting included in FIVECALF, it was 326 (for 330 data points). Figure 11 is the fully crystallized spectrum of Run 4, and except for total intensity, it is nearly identical to Fig 9 (Run 3 at the same temperature). Figures 12 and 13 show the poorly resolved spectra obtained when using AC power for the heater. Sample motion induced by an alternating magnetic field caused extreme line-broadening which resulted in overlapping of the absorption lines. Figures 14 and 15 are two spectra obtained with Fe$_{80}$P$_{6.5}$C$_{3.5}$B$_{10}$ (Run 7). Although the intensity of the $\alpha$-Fe peak of Fig 14 indicated a fully crystallized state, visual inspection of these two spectra show a substantial change.

The crystallized fractions for Fe$_{80}$B$_{20}$ (Runs 1 thru 5) are plotted against time in Fig 16. Representative error bars are indicated on the first and last points of the 626 K data. The data of Run 4 were plotted such that the first data point fell on the calculated Run 3 line. Had the third data point been plotted on this line, the remaining points would have fallen very close to the Run 3 data. Because of low counts and line-broadening of the Mossbauer spectra of Run 2, only the last three data points were useable, and are included in Fig 16. The crystallization half lives, determined from least-squares fits to the data of Fig 16 (between $x = 0.1$ and $x = 0.80$), are plotted versus time in Fig 17. The value of the activation energy $E_A$ for $\alpha$-Fe crystallization was determined
Fig 16. Crystallized Fraction $x(t)$ vs Time, Plotted as $\ln \ln(1/(1-x))$ vs $\ln t$
Fig 17. Arrhenius Plot. Crystallization half lives of Fe$_8$O$_{16}$ versus time, plotted as ln $t_{1/2}$ vs 1000/T
(with 1o error bars)
from a least-squares fit to the data of this Arrhenius plot. The value of $E_A$ was $0.256 \pm 0.006$ MJ/mole ($2.65 \pm 0.027$ eV/atom), and $\ln k_0^{-1}$ was $-47.5$. Using these constants and $T = 473$ K in Eq (3), the predicted half-life of this Fe$_{80}$B$_{20}$ sample is $5500 \pm 450$ years at the expected operating temperature of 473 K.

The Fe$_{80}P_{6.5}C_{3.5}B_{10}$ did not crystallize at 614 K, but crystallized extremely fast at 716 and 744 K. Only one or two spectra were taken before full crystallization at these two temperatures. Hence, no kinetic data were obtained for this material. Only qualitative statements can be made about the crystallization of Fe$_{80}P_{6.5}C_{3.5}B_{10}$; these will be presented in the following section.

Discussion

The values of Chi-squared obtained when analyzing the Mossbauer spectra of Runs 1 through 5 varied over a large range—from less than the number of data points for some runs to up to four times the number of data points for others. This indicates a failure of the mathematical model used to describe the Mossbauer spectra. However, this failure was expected, considering the large number of constraints on the model used for FIVECALF (the values of Chi-squared for the GAUSSCALF and ALPHA-BG fits were generally very close to the number of data points). By visual inspection, the fits were good in the area of the $\alpha$-Fe peaks, and its growth was probably followed accurately. The same cannot be said for the growth
of Fe$_3$B, due to the change in the hyperfine field and FWHM during crystallization. Since the glass spectrum does broaden slightly during crystallization, it may continue to change throughout the transformation. The fit to the Fe$_3$B spectra would then have to account for this change. An alternative view might be to consider the Fe$_3$B as still semi-amorphous during crystallization.

In Mossbauer spectra taken during early annealing runs, the values of FWHM for the Fe$_3$B peaks increased for peaks farther from the center. This is typical of glass spectra (Ref 16: 821). For the fully crystallized spectra, the FWHM's were nearly constant, which indicates a crystalline state. This view tends to support Kemeny's (Ref 10: 485) and Schaafsma's (Ref 11: 4429) conclusions that crystal nuclei exist in the as-quenched glass and that the structure should be based on a locally distorted, quasi-crystalline Fe$_3$B. It appears that the material is transformed from a glass to a semi-amorphous Fe$_3$B, and finally to a tetragonal Fe$_3$B crystal. This may be due to a stress relaxation rather than a crystallization process.

Because of the long time required to reach full crystallization at 573 K, Run 1 was terminated at 315 hrs, and the temperature was raised to 611 K. This was done to try to detect a change in the crystallization process at the lower temperature. The first crystallization time of Run was adjusted by $\Delta t$ so that this data point fell on the line calculated for Run 3. The other times of Run 4 were then adjusted by this
and the data was compared to that of Run 3. Because of the data scatter, no conclusion was made concerning a change in the crystallization rate or process.

Using the methods described in Chapter I, others have found the activation energy of Fe$_{80}$B$_{20}$ to be between 0.195 and 0.257 MJ/mole, with the average toward the upper value (Refs 3: 42; 6: 139; 10: 485; 11: 4427). This range is significant: Luborsky, using calorimetric and magnetic methods to measure the onset of crystallization in Fe$_{80}$B$_{20}$, determined that the activation energy was 0.202 MJ/mole. He used this value to calculate an expected lifetime of 25 years at 473 K. He determined that "after the onset of crystallization, the magnetic properties deteriorate catastrophically [Ref 3: 139]."

Schaafsma determined that the onset of crystallization corresponds to a crystallized fraction of less than 0.02 (Ref 11: 4425). Using his data, with $E_A = 0.242$ MJ/mole, to calculate the onset of crystallization, the projected lifetime of his glass is 1000 years at 473 K. The same calculation yields a lifetime of 400 years at 473 K for the Fe$_{80}$B$_{20}$ of this study. These calculations assume that the crystallization rate is determined by the growth of α-Fe, not Fe$_3$B; and that the crystallization mechanism does not change between 573 and 473 K.

The data obtained during the crystallization of Fe$_{80}$P$_{6.6}$C$_{3.5}$B$_{10}$ were insufficient for analysis of its crystallization kinetics. However, a much higher temperature was required for crystallization. Therefore, qualitatively, its activation energy would be greater than that of Fe$_{80}$B$_{20}$. This
is true for other similar glasses with many atomic species, (i.e., Fe$_{40}$Ni$_{40}$B$_{20}$, Fe$_{80}$P$_{15}$C$_7$, Fe$_{40}$Ni$_{40}$P$_{14}$B$_6$, Ref 3: 140). Thus, the lifetime of Fe$_{80}$P$_{6.5}$C$_{5.5}$B$_{10}$ is expected to be greater than that of Fe$_{80}$B$_{20}$. 


V. Conclusions and Recommendations

The metallic glasses Fe$_{80}$B$_{20}$ and Fe$_{80}$P$_6$C$_3$.5B$_{10}$ have been crystallized by isothermal annealing at high temperatures. The crystallization was followed with Mossbauer spectroscopy, and the rates of formation of α-Fe crystals in Fe$_{80}$B$_{20}$ were determined. These rates were used to determine the activation energy and rate constant of the crystallization process. These constants were used to calculate the expected lifetime of Fe$_{80}$B$_{20}$ at 473 K, 100 K below the lowest isothermal run. If the crystallization mechanism does not change between 473 and 573 K, the onset of crystallization is projected to be approximately 400 years. No kinetic data were obtained for the crystallization of Fe$_{80}$P$_6$C$_3$.5B$_{10}$, or for the formation of Fe$_3$B in the Fe$_{80}$B$_{20}$.

Recommendations

This study can be expanded in the following ways:

1) Use a stronger Mossbauer source to increase counts per channel. This would permit a more careful study of the crystallized spectra to determine Fe$_3$B growth rates.

2) Use an accurate temperature controller (with direct current), and continue the study at lower temperatures.

3) Study the magnetic and material properties of partially crystallized samples. This would relate crystallized fraction to material performance.
Since an alternating field can accelerate the aging of the glass (Ref 12), include a strong rf field during some of the isothermal annealing runs. The field strength must be great enough to displace the atoms in the amorphous metal. Kopcewicz found that 800 A/M at 67 MHz was enough to cause crystallization, but 400 A/M at 53 MHz was not.
Bibliography


SUBROUTINE CALFUN(NP,NPAR,F,X)

THIS VERSION OF CALFUN USES A GAUSSIAN LINE SHAPE TO FIT THE
ABSORPTION SPECTRUM OF A METALLIC GLASS. IT GIVES ONE AVERAGE
VALUE FOR HYPERFINE FIELD, ONE FOR ISOMER SHIFT, AND ONE FOR
QUADRUPOLE SPLIT. IT GIVES A LINEWIDTH FOR EACH OF THE SIX
PEAKS, AND THE INTENSITY RATIO OF PEAK 2 TO PEAK 1. THE AREAL
RATIO FOR PEAKS 3 AND 4 TO PEAK 1 IS 1:3. THESE VALUES CAN
THEN BE SUBSTITUTED INTO THE CALFUN CALLED FIVECALF, TO PERMIT
FITTING THE CRYSTALLIZED GLASS SPECTRA.

GAUSSCALF 15 OCT 80

THE REQUIRED VARIABLES ARE:

ONE VALUE FOR H-FIELD: X(1)

ONE VALUE OF ISOMER SHIFT: X(2)

ONE VALUE OF QUAD SPLIT: X(3)

ONE VALUE FOR TOTAL INTENSITY OF PEAK 1: X(4)

ONE VALUE FOR RELATIVE INTENSITY TO PEAK 1: X(5)

SIX VALUES OF LINE WIDTH: X(6) TO X(11)

BASELINE IS LAST VARIABLE: X(12)

TOTAL OF 12 VARIABLES REQUIRED

COMMON /HEADER/TITL(18)
COMMON /XAM/XINIT(25), PRH(25), ERX(25), NBASE
COMMON /CALF/IFLAG
COMMON /F(4:0), X(25)
REAL V(0), XVEK, XUGND, XSUBN, LIGHT
LOAD VALUES OF BINOMIAL PROBABILITIES

\[ \text{MU} = 1.5491 \]
\[ \text{SIG} = 0.904206 \]
\[ \text{R} = \frac{\text{MU}}{\text{SIG}^2} \]

FACTOR CONVERTS FROM ENERGY UNITS TO VELOCITY UNITS.

\[ \text{GZERO} \times \text{HUSJRN} \times \text{LIGHT} \times \text{F1} \times \text{F2} \]
\[ \text{FACTOR} = \frac{\text{GZERO} \times \text{HUSJRN} \times \text{LIGHT} \times \text{F1} \times \text{F2}}{2 \times \text{EZERO} \times \text{F3}} \]

\[ \text{GZERO} = 1.0848 \]
\[ \text{HUSJRN} = 6.05E-27 \]
\[ \text{LIGHT} = 2.99792458 \]
\[ \text{F1} = 1.0000 \]
\[ \text{F2} = 1.0000 \]
\[ \text{F3} = 1.0000 \]
\[ \text{FACTOR} = \frac{(\text{GZERO} \times \text{HUSJRN} \times \text{LIGHT} \times \text{F1} \times \text{F2})}{(\text{EZERO} \times \text{F3}^2)} \]

\[ A = \text{FACTOR} 	imes (3 \times \text{R} - 1) \]
\[ B = \text{FACTOR} 	imes (\text{R} - 1) \]
\[ C = \text{FACTOR} 	imes (\text{R} + 1) \]

\[ \text{IF}(\text{FLAG} = 25, 25, 14) \]

I have to not positive CALFUN is being called for printing only

\[ \text{CONTINUE} \]

CALCULATE PEAK VELOCITIES FOR EACH SITE

\[ s = x(2) \]
\[ c = x(3)/2 \]
X(1) = ABS(X(1))
Y(1) = A*X(1) + S + Q
Y(2) = D*X(1) + S - Q
Y(3) = -C*X(1) + S - Q
Y(4) = C*X(1) + S - Q
Y(5) = -D*X(1) + S + Q

33   X(I) = APS(X(I))
25   CONTINUE

C CALCULATE THE SPECTRUM
C
RE=L=X(5)*X(7)/X(6)
TF(RE=6.;.1.+4.) X(5)=1.4*X(6)/X(7)
DO 35 I=1, N
      'C(I)=9
      35   K=1,6
      IF(K.EQ.1) TI=X(1)
      IF(K.EQ.2) TI=X(4)*X(5)
      IF(K.EQ.3) TI=X(5)*X(6)/(3.*X(8))
      IF(K.EQ.4) TI=X(4)*X(6)/(3.*X(3))
      IF(K.EQ.5) TI=X(4)*X(9)*X(7)/X(11)
      IF(K.EQ.6) TI=X(4)*X(6)/X(11)
      WW=X*K
      YYY=(YD(I)-V(K))*2/(2.*X(KP5)*.4247*X(KP5)*.4247)
      TF(YYY.5F.14+) YYY=1.0

      35   YD(I) = YD(I) +(1/32.*X(KP5)*X(KP5)*.4247*.4247)*EXP(-YYY)
      YC(I) = (1.+YD(I)) *X(NBASE)
      IF(I.EQ.1) F(I) = YD(I) - YC(I)
      IF(I.EQ.2) F(I) = YD(I) /SORT(YD(I))
      CONTINUE
C
C ON THE FINAL CALL OF CALFUN PRINT THE PEAK VELOCITIES
C
25   CONTINUE
PRINT 90

PRINT "THE PEAK VELOCITIES ARE:
PRINT 100, (V(I), I=1, 6)
PRINT "
PRINT "
61 FORMAT (1H1)
100 FORMAT (5X, 7F14.4)
RETURN
END
SUBROUTINE CALFUN(NP,NPAR,F,X)

CALFUN USES SUPERPOSITION OF FIVE 5-PEAK SPECTRA: ONE FOR
ALPHA-Fe, THREE FOR FE3B, AND ONE FOR THE GLASS. THE VARIABLE
PARAMETERS ARE LISTED BELOW. THE LINWIDTH FOR ALPHA-Fe MUST
BE ADDED AT LINE 173. AREA RATIOS ARE NORMALIZED TO PEAK 1
FOR EACH SPECTRUM. ALL THREE FE3B SPECTRA ARE REQUIRED TO HAVE
THE SAME AMPLITUDE, AND AREA RATIOS FOR PEAKS 1:2:3:4:5:6 OF
1:2:1:1:2:3. FOR THE GLASS SPECTRUM, ONLY THE INTENSITY IS A
VARIABLE PARAMETER, THE OTHERS MUST BE SUPPLIED IN LINES 149
TO 161 AND 182 TO 192. THIS CALFUN ALSO GIVES THE COUNTS
ABSORBED BY ALPHA-Fe AND THE TOTAL COUNTS ABSORBED. THIS VERSION
OF FIVECALF IS FOR 336 C DATA ONLY.

FIVECALF 22 NOV 80

THE REQUIRED VARIABLES ARE:

ONE VALUE OF H-FIELD FOR ALPHA IRON: X(1)
THREE VALUES OF H-FIELD FOR FE3B: X(2) TO X(4)
ONE VALUE OF TOTAL INTENSITY FOR ALPHA Fe: X(5)
ONE VALUE OF TOTAL INTENSITY FOR FE3B: X(6)
THREE VALUES OF LINWIDTH FOR FE3B: X(7) TO X(9)
ONE VALUE OF ISOMER SHIFT FOR ALPHA Fe: X(10)
THREE VALUES OF ISOMER SHIFT FOR FE3B: X(11) TO X(13)
ONE VALUE OF TOTAL INTENSITY FOR THE FE3B20: X(14)
BASELINE IS LAST VARIABLE: X(15)
TOTAL OF 15 VARIABLES REQUIRED
COMMON W(13*1), XD(402), YD(402), Y2(402), YDY(402), YCY(402), FSD(402), I2.5
COMMON /HEADING/TITL(18)
COMMON 2 3AM, XNIT(25), PRM(25), ERX(25), NNAME
COMMON /CALF/IFLAG
DIMENSION F(402), X(25)
REAL V(31), MU, EM, MUSUBM, MUSUBN, LIGHT, H, B1(5)

MU: X = 1.1.91
MUSUBN = 1.912(E)
R = MUX/(MUSUBN*3.)

FACTOR CONVERTS FROM ENERGY UNITS TO VELOCITY UNITS.

GZERO*MUSUBN*LIGHT*F1*F2
FACTOR = ------------------------
2.*EZERO*F3

GZERO = 1.1.048
MUSUBN = 5.65E-27
LIGHT = 2.696E11
F1 = 1.6E3
F2 = 1.9E-6
FZERO = 1.4.125E3
F* = 1.6.325E-19

FACTOR = (GZERO*MUSUBN*LIGHT*F1*F2)/(EZERO*F3*2.)

IF (IFLAG) 25, 25, 1

C IF IFLAG IS NOT POSITIVE CALFUN IS BEING CALLED FOR PRINTING ONLY
CONTINUE

CALCULATE PEAK VELOCITIES FOR EACH SITE

DO 11 I=1,9
11 X(I)=ABS(X(I))

THE FOLLOWING IS FOR THE ALPHA IRON SPECTRUM.
H IS THE HYPERFINE FIELD AND S IS THE ISOMER SHIFT.
V(1) TO V(6) ARE THE VELOCITIES OF PEAKS ONE TO SIX.

H=X(1)
S=X(7)
V(1)=A*H+S
V(2)=C*H+S
V(3)=-C*H+S
V(4)=C*H+S
V(5)=-D*H+S
V(6)=-A*H+S

THE FOLLOWING IS FOR THE FIRST FE33 SPECTRUM.

H=X(2)
S=X(11)
V(7)=A*H+S+Q
V(13)=0*H+3-Q
V(19)=-C*H+S-Q
V(25)=C*H+S-Q
V(31)=D*H+S-Q
V(41)=-A*H+S+Q

THE FOLLOWING IS FOR THE SECOND FE33 SPECTRUM.

H=X(3)
THE FOLLOWING IS THE THIRD Fe38 SPECTRUM.

\[ H = \chi(13) \]

\[ S = \chi(12) \]

\[ V(11) = A * H + S + O \]

\[ V(12) = A * H + S - O \]

\[ V(21) = C * H + S - O \]

\[ V(22) = C * H + S + O \]

\[ V(13) = A * H + S + O \]

\[ V(14) = A * H + S - O \]

\[ V(23) = C * H + S - O \]

\[ V(24) = C * H + S + O \]

\[ V(15) = - A * H + S + O \]

\[ V(16) = - A * H + S - O \]

THE FOLLOWING IS THE Fe80Cr22 GLASS SPECTRUM; IT MUST BE CHANGED TO MATCH THE NON-CRYSTALLIZED GLASS SPECTRUM FOR A GIVEN TEMPERATURE.

\[ H = 45^\circ \]

\[ S = - 2^\circ \]

\[ O = - 47^\circ \]

\[ V(25) = A * H + S + O \]

\[ V(26) = A * H + S - O \]

\[ V(27) = C * H + S - O \]

\[ V(28) = C * H + S + O \]

\[ V(29) = O * H + S - O \]

\[ V(30) = O * H + S + O \]

CONTINUE

CALCULATE THE SPECTRUM

\[ A^E = \pi L \]

\[ A^T = \pi L \]

DO 31 I = 1, NP

IF(I.LE.150 .OR. I.GE.151) GO TO 31
YD(I)=1-(.5*YD(I-1)+.35*YD(I+1)+.39*YD(I))/X(NBAS)

GO TO 31

YD(I) = 1

IF K = 1, 3

IF (K.EQ.1 OR K.EQ.6) T1=X(5)

IF (K.EQ.2 OR K.EQ.5) T1=X(5)*2/3.

IF (K.EQ.3 OR K.EQ.4) T1=X(5)/3.

IF (K.EQ.6 AND K.LT.13) T1=X(5)

IF (K.EQ.12 AND K.LT.19) T1=X(5)*X(7)*2/3/X(8)

IF (K.EQ.18) T1=X(6)*X(7)/3/X(3)

IF (K.LT.7) P1=1.36

IF (K.EQ.13) B=X(7)

IF (K.EQ.12 AND K.LT.19) B=X(7)

IF (K.EQ.18 AND K.LT.25) B=X(9)

IF (T.EQ.24) GO TO 32

YDP=T1/(((XD(I)-V(K))*2*4.)/9**2)+1.)

GO TO 73

32

TI1=AES(X(14))

THE FOLLOWING ARE THE LINWIDTHS OF THE SIX GLASS PEAKS.

P1(1)=2.4

P1(2)=1.04

P1(3)=1.38

P1(4)=1.25

P1(5)=1.76

P1(5)=2.59

IF (K.EQ.25) T1=TI1

THE 1.3' IN THE FIRST AND FOURTH LINES FOLLOWING IS THE INTENSITY RATIO OF PEAK 2 TO PEAK 1 (OF THE GLASS).

IF (K.EQ.26) T1=TI1*1.3*P1(1)/P1(2)

IF (K.EQ.27) T1=TI1*3.1*P1(1)/P1(3)

IF (K.EQ.28) T1=TI1*8.1*P1(1)/P1(4)

IF (K.EQ.29) T1=TI1*1.3*P1(1)/P1(5)

IF (K.EQ.30) T1=TI1*8.1*P1(1)/P1(6)

YYY=(XO(I)-V(K))*2+3667/P1(K-24)**2

IF (YYY.GT.14.) YYY=10.50

50
YCP = \( (T^I/\text{SORT}(1.133*31(K-24)+2)) \times \exp(-YY) \)

**CALCULATE COUNTS ABSORBED BY ALPHA-Fe.**

15 \( I \leq K \): AAFE = AAFe + YCP

30 \( Y^C(I) = YC(I) + YCP \)

**CALCULATE TOTAL COUNTS ABSORBED.**

35 \( S^T(S) = ATOT + YC(I) \)

36 \( Y^C(I) = (1 - YC(I)) \times \text{NBASE} \)

38 \( F(I) = (YD(I) - YC(I)) / \text{SORT}(YD(I)) \)

**ON THE FINAL CALL OF CAFUN PRINT THE PEAK VELOCITIES AND THE COUNTS ABSORBED.**

92 FOR \( I = 1,10 \), THE PEAK VELOCITIES ARE (IN mm/sec): 1, 12

PRINT 1, (V(I), I = 1, 6)

PRINT 93

93 FOR \( I = 1,3 \), THE PEAK VELOCITIES FOR THE THREE Fe3+ SPECTRA ARE: 22, 33

PRINT 1, (I = 1, 11, 2)

PRINT 1, (V(I), I = 12, 13, 7, 11)

**END**
SUBROUTINE CALFUN(NP,NPAR,F,X)

THIS CALFUN FITS ONLY PEAKS ONE AND SIX OF THE ALPHA-Fe SPECTRUM.
IT ADDS A GAUSSIAN-SHAPED BACKGROUND TO THE ALPHA-Fe TO ACCOUNT FOR
THE CLOSURENESS OF THE GLASS SPECTRUM AND THE CRYSTALLIZED ALPHA-Fe
SPECTRUM. IT FITS THE CENTER PORTION OF THE SPECTRUM WITH THE
APPROXIMATE DATA VALUES.

ALPHA-Fe 22 OCT 81

THE REQUIRED VARIABLES ARE:

ONE VALUE OF H-FIELD FOR ALPHA IRON: X(1)
ONE VALUE OF H-FIELD FOR THE BACKGROUND CURVE: X(2)
ONE VALUE OF ISOMER SHIFT FOR ALPHA IRON: X(3)
ONE VALUE OF ISOMER SHIFT FOR THE BACKGROUND CURVE: X(4)
TWO VALUES OF LINE WIDTH: X(5) TO X(5)
ONE VALUE OF TOTAL INTENSITY OF PEAK 1: X(7)
FOR ALPHA IRON
ONE VALUE OF TOTAL INTENSITY OF THE BACKGROUND: X(8)
BASELINE IS LAST VARIABLE: X(9)
TOTAL OF 9 VARIABLES REQUIRED

COMMON W(1300), X0(402), YD(402), YD(402), YD(402), YC(402), FC(402), J(4)1427
COMMON /HEADING/TITL(18)
COMMON /NAH/XINIT(25), PRM(25), ERX(25), NBASE

COMMON /CALF/ IFLAG
DIMENSION F(2),X(25)
REAL V(6),MUEX,MUGNO,MUSUBN,LIGHT

LOAD VALUES OF BINOMIAL PROBABILITIES

MUEX=.15891
MUGNO=-.09.1216
R=MUEX/(MUGNO*3.)

FACTOR CONVERTS FROM ENERGY UNITS TO VELOCITY UNITS:

GZERO=MUSUBN*LIGHT*F1*F2
FACTOR = ----------------------
2. *GZERO*F3

GZERO=.16548
MUSUBN=5.255E-27
LIGHT=2.99792411
F1=1.*F3
F2=1.*F4
F3=1.*F5
F4=1.*F6
F5=1.*F7
F6=1.*F8
F7=1.*F9
F8=1.*FACTOR
F9=1.*FACTOR
FACTOR=(GZERO*MUSUBN*LIGHT*F1*F2)/(GZERO*F3*2.)

A = FACTOR*(Z.*R-1.)
B = FACTOR*( R-1.)
C = FACTOR*( F+1.)

IF(IFLAG)25,19,1
IF IFLAG IS NOT POSITIVE CALFUN IS BEING CALLED FOR PRINTING ONLY
CONTINUE
C CALCULATE PEAK VELOCITIES FOR EACH SITE

DO 11 I=1,2
11 X(I)=APS(X(I))
V(1)=A*X(1)+X(3)
V(2)=A*X(2)+X(1)
V(3)=A*X(3)+X(1)
V(4)=A*X(2)+X(1)
V(5)=A*X(1)+X(3)
DO 33 I=3,4
33 X(I)=APS(X(I))
CONTINUE

C CALCULATE THE SPECTRUM

TAFF=0.
ATOT=0.
DO 95 I=1,NF
IF(I,LT,32 OR, I.GT,214) GO TO 31
Y(I)=1-(5)*YD(I-1)+.55*YD(I+1)+.39*YD(I)/X(NBASE)
GO TO 76
31 Y(I)=0.
DO 37 K=1,6
IF(K.EQ.1 OR K.EQ.4) TI=X(7)
IF(K.EQ.2 OR K.EQ.3) TI=X(8)
IF(K.EQ.2 OR K.EQ.3) GO TO 32
YCP=T*(1+((XD(I)-V(K))*2+4.0)/X(5)*2+1.0)
TAFF=TAFF+YCP
GO TO 76
32 YYY=(XD(I)-V(K))*2/(2.*(.42+7*X(5)))*2)
IF/YYYY.GT.10.0 YYYY=10.0
YCP=T/SORT(.5+2830/.4247/X(5))*EXP(-YYYY)
35 YC(I)=Y(I)+YCP
36 ATOT=ATOT+YC(I)
GO TO 76
RETURN

C ON THE FINAL CALL OF CALFUN PRINT THE PEAK VELOCITIES

CONTINUE
PRINT AE
PRINT *, " "
PRINT *, " "
PRINT *, " THE PEAK VELOCITIES ARE:"
PRINT *, " "
PRINT 14, (V(I), I=1,4)
PRINT *, " "
PRINT *, " "
PRINT *, "THE AREA UNDER PEAKS 1 AND 5 OF ALPHA IRON IS: AAFE
PRINT *, " THE TOTAL ALPHA IRON AREA IS TWICE THAT AREA:"
PRINT *, " "
PRINT *, " "
PRINT *, "THE AREA UNDER THE ENTIRE CURVE IS: ATOT
PRINT 96
30 FORMAT(1H1)
101 FORMAT(5X,F1(4))
RETURN
END
APPENDIX D

GENFIT Instructions

This appendix contains instructions for using GENFIT with one of the three CALFUNs listed in Appendices A, B, and C. It is presented in two parts; the first explains the control cards and parameters used when running GENFIT, the second describes how to alter FIVECALF for different temperature runs.

Control Deck

The following control deck precedes the data. It permits processing on the AFIT terminal only.

DEB,T300,CM120000.STCSB. M7999999,DELLER,4369.
ATTACH,7,GENFIT,MR=1
FIN,1=1,OPT=0,R=2,i=0.
ATTACH,COMPFILE,GAUSSCALF,MR=1
FIN,1,OPT=0,R=2,L=0.
ATTACH,P,CCPLOT5X,ID=LIBRARY,SN=ASD.
LIBRARY,P.
LDSET,PRESET=ZERO
LGO.
7/8/9

The first two cards of the data deck are title cards. They are used to identify the material and run number, and the CALFUN used for processing the data. The third data card contains processing parameters as explained below.
The parameter cards then follow this card. In this case, there are twelve (as in above card). Two are given for example (format I6, open):

```
HFIELD  310.
  .
  .
  .
  .
BASELN  52000
```

The Mossbauer data deck follows immediately after the parameter cards. There are forty data cards, in 13, 1017 format. They contain the channel number of the first data entry on each card plus 10 channels of data. The final two cards contain more processing parameters.
The final card for processing Mossbauer data is the end-of-job card:

6/7/8/9 END OF JOB

Altering FIVECALF

FIVECALF must be changed for different temperature runs because the glass spectrum changes over a given temperature range. The average hyperfine field, the distribution of fields, the relative intensity of peak two to peak one, and the isomer shift and quadrupole split all vary with temperature. Altering FIVECALF is rather simple, however. Once CAUSSCALF has been run with a non-crystallized spectrum and the parameters
They are listed below by line number in Appendix B.

000220 change temperature to that which this copy of FIVECALF will be for

001460 change H=145. to the hyperfine field obtained with GAUSSCALF

001470 change S=-.200 to the isomer shift obtained

001480 change Q=-.005 to the quadrupole split obtained

001840 change B1(1) to the value obtained for the linewidth of peak one

001850 change B1(2) to the value obtained for the linewidth of peak two

001860 change B1(3) to the value obtained for the linewidth of peak three

001870 change B1(4) to the value obtained for the linewidth of peak four

001880 change B1(5) to the value obtained for the linewidth of peak five

001890 change B1(6) to the value obtained for the linewidth of peak six

001950 change 1.30 to the value of the ratio of peak two to peak one

001980 change 1.30 to the value of the ratio of peak two to peak one
APPENDIX E

Applications of Metallic Glasses

In this appendix some of the existing and proposed applications of the metallic glasses are described. The mechanical, electrical, and magnetic properties of some of the glasses make them suitable for many uses. Two commercial applications have existed since 1976. A woven fabric has been manufactured for use as magnetic shielding. It performs as well as Fe$_{80}$Ni$_{20}$ foil, and it has the advantage of high flexibility. The other current application of metallic glass is in magnetostrictive delay lines, which take advantage of the large magnetostriction of the metallic glasses and the high change in Young's modulus with applied magnetic field. Other uses are envisioned which take advantage of various combinations of magnetic "softness," mechanical hardness, and high electrical resistivity.

Due to the ease of reversing magnetic fields in the metallic glasses, power transformers with these materials in their cores would lose much less energy to heating. These glassy metals have been proposed for winding the cores of inversion transformers, current and pulse transformers, and magnetic amplifiers. They also are likely candidates for the "read" and "write" heads in magnetic tape recorders and disc
metal systems. Their electrical resistance properties make them suitable for electrical resistors, low temperature heating wires, and resistance thermometers.

The various mechanical properties of the glassy metals make them useful for many other applications. Because of high tensile strength, some of the glasses might be used as reinforcing filaments in tires, transmission belts, or high pressure tubing; or as stress transducers in a multivibrator configuration. Their corrosion resistance makes them useful in underwater cables or biomaterials. The hardness and ability to be sharpened make some of the glassy metals suitable materials for manufacturing cutting devices.

Besides the above applications which are based on the macro-properties of the metallic glasses, there is at least one use based on their micro-structure: they have been proposed as the storage medium for magnetic "bubble" memory systems. Since the bubbles in the metallic glasses are one-fifth the size of those in synthetic garnet, the storage density would be 25 times greater. The vortices (important in superconductors) are 10 times smaller. If these can be used for storage, the information density could be 250 times greater than that now projected in synthetic garnet bubble memory systems.

All of the above applications can take advantage of two common properties of the metallic glasses: they are very easy to work with, due to their flexible-fiber form; and they are inexpensive to manufacture, due to the one-step production
prec., with no subsequent treatments necessary. A few of the authors who have researched the applications of the metallic glasses—and will probably continue—are: C.D. Graham, T. Egami, J.J. Gilman, P. Chaudhari, and F.E. Luborsky.
Vita

Denis Eugene Beller was born on November 22, 1950, in Okmulgee, Oklahoma, and is the son of Ernest E. and Ezma I. Beller. He graduated from Norte Del Rio High School in Sacramento, California in June 1968. He attended the University of Nevada and American River College before enlisting in the Air Force in 1971. In May 1976 he graduated with honors from the University of Colorado with a degree of Bachelor of Science in Chemical Engineering. Following graduation from Air Force Officer Training School, he served as a test engineer at the Air Force Rocket Propulsion Laboratory, Edwards AFB, California. Prior to attending the Air Force Institute of Technology, he served as a test section chief and senior test engineer at Edwards. He and his wife Judy have two sons.

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In this study, Mossbauer spectroscopy was used to examine thermal aging of two metallic glasses. Fe<sub>80</sub>B<sub>20</sub> was isothermally annealed at 573, 604, 611, and 626 K and Fe<sub>80</sub>B<sub>20</sub>P<sub>5</sub> was annealed at 614, 716, and 744 K. The activation energy of Fe<sub>80</sub>B<sub>20</sub>, determined from the growth of...
α-Fe crystals, was 0.256 ± 0.006 MJ/mole. The projected lifetime of this glass, based on the onset of crystallization, is 400 years. No quantitative data were obtained for Fe₈₀₋₆.₅C₆.₅B₁₀; however, based on the higher temperature required for crystallization, it is expected to have a longer lifetime.