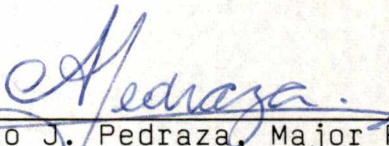
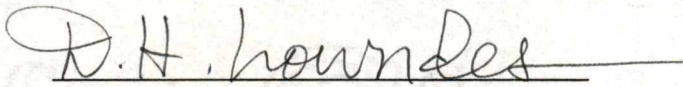
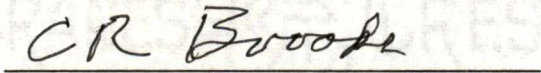


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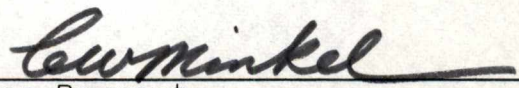
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AMORPHIZATION OF IRON-BORON ALLOYS
BY EXCIMER LASER PROCESSING

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

James W. McCamy

December 1987

DEDICATION

This work is dedicated to my parents

Eve and Mac

and

my wife and best friend

Ann

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ABSTRACT

Samples of crystalline iron-boron alloys containing 5-30 at%B were processed by irradiating them with slightly overlapping single pulses from a XeCl excimer laser to study the extent to which amorphization occurs at extremely high heating and cooling rates. The influence of the initial microstructure and phases upon the structure that results after laser processing was also studied.

A surface sensitive x-ray diffraction (SSXD) technique was developed to study the structural changes in the modified near-surface region. With this technique both the melt depth and the volume fraction of crystalline material present in the amorphous layer could be determined. The layer was further characterized using a grazing angle diffraction geometry.

The specimens were prepared using the hammer and anvil method of splat quenching. It was found that the initial microstructure could be determined by controlling the sample weight. An amorphous structure was obtained with sample weights less than 0.04 grams, while fully crystalline structures were produced when the sample weight was greater than 0.08 grams.

Amorphization was observed when as-quenched Fe-B alloys with 10-30 at%B were processed with the excimer laser. However, only those samples with 15-20 at%B showed

complete amorphization; all other compositions showed only partial amorphization. Processing of as-quenched Fe-5at%B alloys produced a bcc phase with a lattice parameter 0.9% less than that of pure iron.

Amorphization was not observed in Fe-B samples which were annealed prior to laser processing. Comparision of the microstructures showed that the grain size of the annealed material was an order of a magnitude larger than that found in the as-quenched material. An analytical diffusion model was developed which showed that the initial microstructure plays a fundamental role during pulsed laser processing inasmuch as compositional inhomogeneities that may remain in the liquid determine the resulting structure. These inhomogeneities occur because the time of diffusion in the liquid state in samples with large grain sizes is insufficient for homogenization to occur. The experimental evidence, together with the developed model, gives 5.3 at%B as the lower limit for amorphization. Extrapolation of experimental data yields an upper limit of 40 at%B.

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INTRODUCTION

While we have been able to produce glasses in such non-metallic materials as borate and silicate compounds for thousands of years, it has only been in this century that technology has reached a point where the production of amorphous metallic materials is feasible. The technology for commercial production of metallic glasses, however, has been available for a much shorter period of time. Therefore, the amount of information known about the metallic systems which exhibit glass forming tendencies, and even those which are easy glass formers, is quite small. This is perhaps unusual since most, if not all, metallic glasses possess properties and qualities which are superior to their crystalline counterparts. Thus, there currently exists a great need to extend our knowledge in many areas of glass formation in metallic systems.

Glasses are solid materials with a certain degree of topological and chemical short-range order but which lack topological long-range order. They are also defined as materials which are formed by the continuous hardening of a cooled liquid without the nucleation and growth found in crystalline materials. Thus, while amorphous metallic materials were formed as early as 1930 by vapor deposition, it was not until 1960 that metallic glasses were first formed. Since that time several different processes for

rapidly quenching metals from the liquid state to an amorphous one have evolved. Melt spinning and centrifugal atomization are the two which are the most widely known processes. In both cases, the molten metal is expelled, under pressure, onto a rotating plate.

In centrifugal atomization, the liquid metal stream breaks into tiny droplets upon impact and is then thrown outward by the centrifugal force supplied by the plate. These droplets then cool rapidly in jets of cold, inert gas blown into the chamber. The fine powder which results may then be consolidated by a hot extrusion process to form a homogenous product.

In the melt spinning process, however, the rotating plate acts as a cold substrate, and the molten stream hardens into a thin ribbon. This amorphous ribbon may then be used without further treatment to take best advantage of its superior properties.

Numerous other methods exist which may be used to produce metallic glasses. However, at this time none are being used commercially. One such method is the hammer and anvil or splat quenching technique. This process appears to have little commercial appeal; however, due to its simplicity, it is widely used in the study of glass forming systems.

Two other methods, quite similar in nature, are laser and electron beam quenching. Both techniques are presently

used commercially to harden and alloy the surfaces of materials, and appear to have the most commercial potential as methods to produce glassy surfaces on materials. They have the advantages of being simple to use and having the ability to process workpieces with randomly shaped, nonplanar surfaces. Further, since only the near surface region is processed, they inherently use less energy than those which transform the entire bulk of the workpiece. Of these two processes, however, electron beam processing requires a vacuum for those workpieces needing a large gun-to-workpiece distance. Moreover, the laser does not require magnetic lenses or directional coils as does an electron beam unit. Therefore, based on initial capital considerations, the laser appears to be more attractive.

Since metallic glasses were first produced in 1960 when Klement, Willens and Duwez rapidly quenched a liquid Au-Si alloy to liquid nitrogen temperature, many other alloys have been produced as metallic glasses. Of the elements known today, almost one-quarter have been found to produce metallic glass alloys. As pointed out by Masumoto and Maddin (1976) metallic glasses are obtained for many transition metal-metalloid (T-M) systems.

Among the LT-M systems, the Iron-Boron alloys exhibit qualities, which, from both a commercial and a research standpoint, make them ideal candidates for study. Therefore, a systematic study of the glass-forming ability of

Fe-B alloys was undertaken in the present work with the purpose of:

1. Determining the effect that composition and micro-structure have on the glass forming ability of Fe-B alloys, when processed by nanosecond excimer laser irradiation.

2. Measuring the thickness of the modified layer as a function of the laser energy flux and evaluating the threshold energy required for melting.

CHAPTER I

METALLIC GLASSES

Several models have been advanced to describe metallic glasses and the phenomenon by which they are formed. Each of these, may be grouped into one of the following categories; (1) structural, (2) thermodynamic, or (3) kinetic.

Structural Models

Various structural models have been presented to date. One model assumed that glasses are composed of clusters of micro-crystals about 20 Angstroms in size. This idea was examined theoretically in considerable detail using various crystal shapes and sizes. However, early researchers were unable to reconcile the model with experimental radial distribution function (RDF) data, and in 1969 the model was "definitively rejected" (Dixmier, 1976).

A second model was proposed about this time when it was noted that the observed RDF data for a Ni-P amorphous alloy was much like that predicted by Finney for the dense random packing (DRP) of hard spheres (Cargill, 1970). The DRP model had first been suggested by Bernal (1960) for simple monatomic liquids but was later applied to polyatomic amorphous metals (Polk, 1970). While the DRP model appears to be applicable to a large number of glass forming

systems (Takayama, 1976), recent RDF data (Frahm, 1984 and Hermann, 1986) indicate this model cannot be applied to the Fe-B system. This will be examined in more detail in the next chapter.

Another model advanced may be viewed as an offshoot of the cluster model. It incorporates the idea of short range, highly ordered regions but suggests that these clusters contain structural elements (e.g. five-fold symmetry) which cannot be the basis of an extended three-dimensional lattice (Hoare, 1971).

A fourth model was developed on the basis of work done on oxide glasses and describes the glass as a network array of structural elements which are randomly arranged such that no unit of the array is repeated at regular intervals in three dimensions (Zachariasen, 1932). It has since been applied to other materials including metals (Chaudhari, 1978 and Uhlmann, 1980).

Although these models provide important descriptions of the structural characteristics of liquids and glasses, and in some cases may provide insights as to why a certain material is a glass former, overall they are rarely applicable in determining the relative ease of glass formation over a broad range of materials.

Thermodynamic Models

Many of the thermodynamic models were developed after it was observed that certain extensive thermodynamic variables (e.g. volume, entropy and enthalpy) are continuous at the glass transition temperature (T_g) while the derivative values (heat capacity, etc.) of these variables are not (Figure 1). In fact, T_g may be defined as the temperature at which these properties are discontinuous. This discontinuity suggests that the transition is a second-order thermodynamic phase transition. However, it has been observed that the temperature at which T_g occurs increases with an increase in the cooling rate. This is contrary to what is observed in other processes which are second-order and would indicate that the formation of metallic glasses is not a true thermodynamic phase transition (Hillert, 1981). Thus, it appears that those models (e.g. excess entropy, etc.) which describe the glass transition in terms of a second-order thermodynamic transition are not correct.

In light of this, Cohen and Grest (1979) extended the kinetic free-volume model (Turnbull, 1970) to include thermodynamic effects as well. Based on this work, they attributed the discontinuity in the differential properties to be a consequence of the system falling out of thermodynamic equilibrium "as the time of measurement becomes

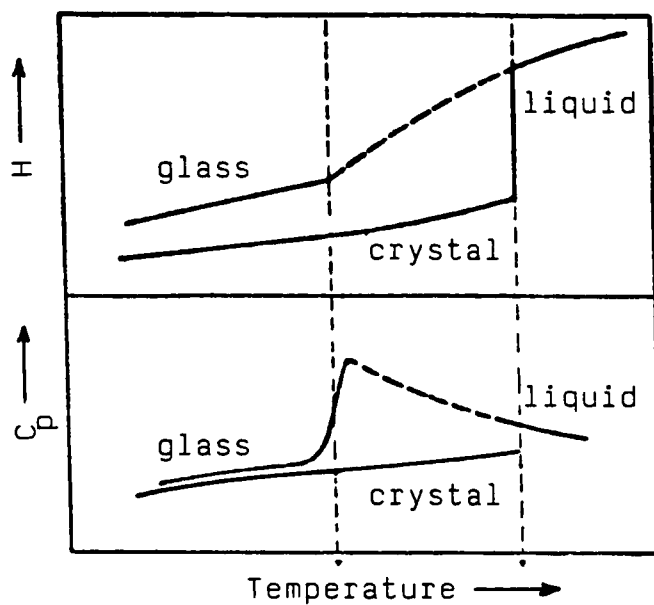


Figure 1. Temperature dependence of the enthalpy H , and specific heat C_p corresponding to crystallization and vitrification of a metallic glass.

comparable to the relaxation times of the system." They further concluded that the glass transition is most probably a first-order transition "in the limit of slow cooling or heating." However, this portion of the model will not be applicable in this study since very high cooling rates are required to produce metallic glasses.

Thus, while thermodynamic models can describe the conditions and limitations under which metallic glasses are prohibited from forming, they do not provide an adequate description of the glass formation process.

Kinetic Models

Crystallization involves two kinetic stages, nucleation and growth. If either is bypassed, the material will remain amorphous when it solidifies. Thus, kinetic models attempt to describe the conditions under which nucleation and/or growth of the crystalline phase will not occur.

In considering nucleation in liquids, Turnbull (1969) noted that the resistance to nucleation "arises from the work, σA , which must be done to form the crystal-liquid interface", where A is the area of the interface and σ is the interfacial energy. The difference in free energy between the crystalline and liquid phases, on the other hand, is the driving force for nucleation. This is a function of the volume of the crystalline phase and thus, when there is little or no compositional difference

between the crystal and the liquid, this may be expressed as the product of the volume of the crystal, V , and the change in free energy per unit volume (Turnbull):

$$\Delta G_v = -\frac{1}{V} \left\{ \Delta H_m \Delta T_r T_m \int_1^{T_r} \left| \int_1^{T_r} \frac{\Delta C_p}{T_r} d T_r \right| d T_r \right\} \quad (1)$$

where ΔH_m is the heat of fusion, ΔC_p is the difference in heat capacity between the crystal and the liquid, and V is the molar volume of the crystal. T_r is the reduced temperature (T/T_m) and ΔT_r is defined as the reduced undercooling $(T_m - T)/T_m$, where T_m is the equilibrium crystallization temperature and T is the actual temperature of the undercooled liquid.

The interplay between the surface and volume energy terms leads to the condition that a certain critical number of molecules must be present in a nuclei for crystal growth to occur. The time required to form this critical nucleus in the liquid is given by:

$$t = i t_j \quad (2)$$

where i is the critical number of molecules and t_j is the average time per molecule for a molecular rearrangement from a random position in the liquid to a crystalline lattice site. Assuming that t_j scales with viscosity and $\Delta C_p = 0$, Turnbull showed that the steady state frequency of nucleation (i.e. constant nucleation rate) is given by

$$I_v = \frac{K_n}{\eta(T)} \exp \left[\frac{-b a^3 \beta}{T_r \Delta T_r^2} \right] \quad (3)$$

where K_h is a kinetic constant, $\eta(T)$ is the viscosity at temperature T , b is a shape constant and α and β are parameters defined as:

$$\alpha = \frac{(NV^2)^{1/3} \sigma}{\Delta H_m} \quad (4)$$

$$\beta = \frac{\Delta S_m}{R} \quad (5)$$

where N is Avogadro's number, R is the gas constant, ΔS_m is the entropy of fusion and σ is the surface free energy. In Figure 2, this upper limiting nucleation frequency is shown as a function of the reduced undercooling and it can be seen that for $\alpha\beta^{1/3} > 0.9$ that homogeneous nucleation is avoided. A Vogel-Fulcher form for the temperature dependence of the viscosity can be assumed (Uhlmann and Yinnon, 1983):

$$\eta = 10^{-33} \exp \left| \frac{3.34}{T_r - T_{rg}} \right| \quad (6)$$

where $T_{rg} = T_g/T_m$. Figure 3 shows, that when this is done, liquids for which $\alpha\beta^{1/3} = 0.5$ and $T_{rg} = 2/3$ should readily form glasses if they are free of heterogeneous nuclei.

If the heat capacity in the liquid and crystal phase is assumed to be constant and equal, the resistance to nucleation is given as BkT^* (Uhlmann, 1983), and the frequency of homogeneous nucleation may then be written as:

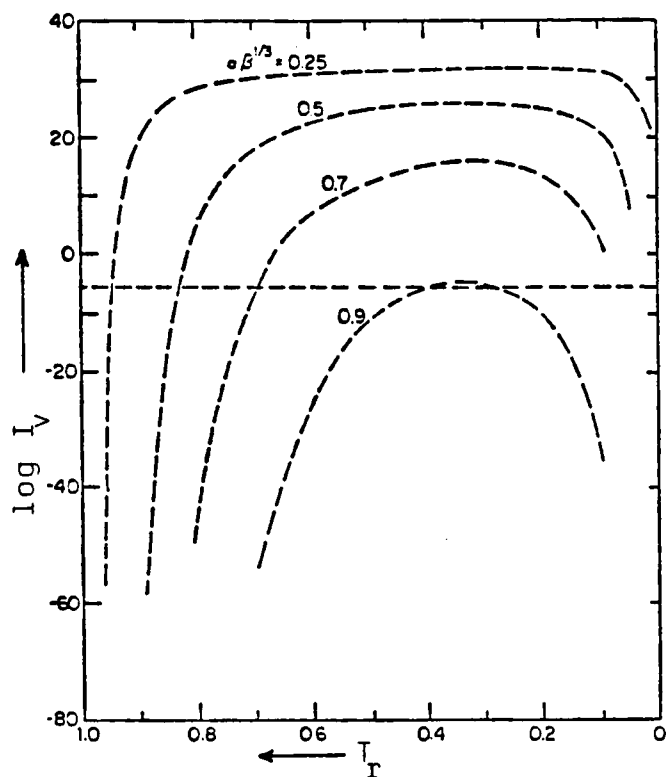


Figure 2. Calculated variation of the logarithm of the frequency (in $\text{cm}^{-3}\text{s}^{-1}$) of homogeneous nucleation of crystals in an undercooled liquid with reduced temperature for various values of $a\beta^{1/3}$. (Turnbull, 1969)

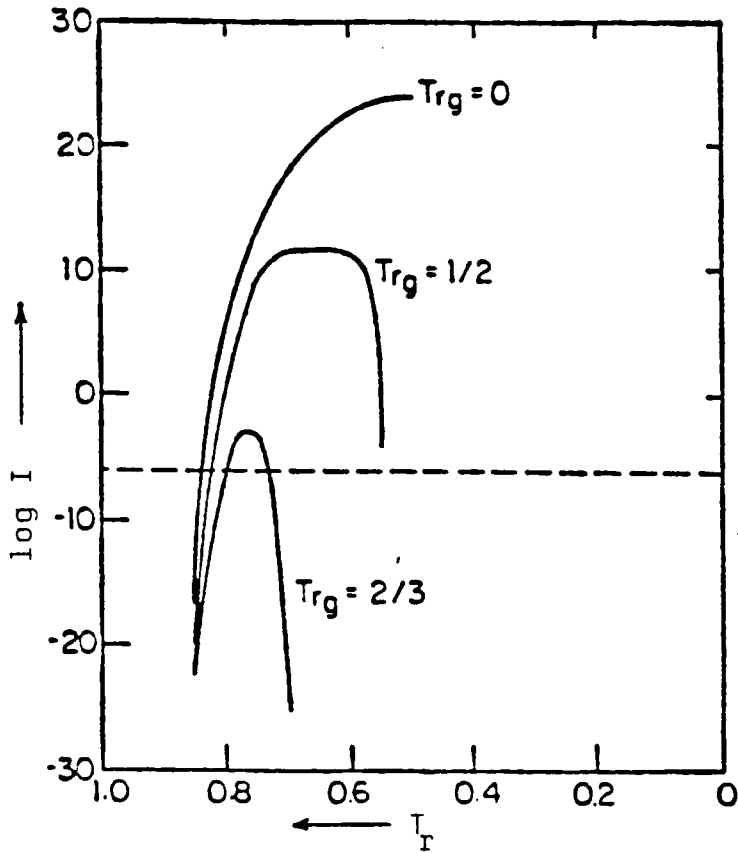


Figure 3. Variation of logarithm of frequency (in $\text{cm}^{-3}\text{s}^{-1}$) of homogeneous nucleation of crystals in liquids with reduced temperature with $\alpha\beta V^2$ set equal to $\frac{1}{2}$ and viscosity calculated from the Fulcher equation. (Turnbull, 1969)

$$I_v = N_v v \exp \left| \frac{-0.0205 B}{\Delta T_r^2 T_r^3} \right| \quad (7)$$

where the mobility, B , is a function of the interfacial energy and free energy difference, k is Boltzmann's constant, T^* is equal to $0.8T_m$, N is the number of molecules per unit volume in the liquid and v is the frequency of atom transport at the interface.

On the other hand if the melt does contain a number (n_v) of active nucleating heterogeneities, then the steady-state frequency of heterogeneous nucleation may be expressed as:

$$I_v = n_v N_v^{23} v A \exp \left| \frac{-0.0205 B \theta}{\Delta T_r^2 T_r^3} \right| \quad (8)$$

where A is the surface area of each heterogeneity and θ is a function of the contact angle between the heterogeneity and the nucleus (Turnbull, 1956).

As heterogeneous nucleation proceeds, the number of active nucleation sites does not remain constant but is depleted. Becker and Doring (1935) have shown that if the crystallization time is short enough, the rate of nucleation is time dependent.

For the case where the melt contains a very large number of heterogeneities (e.g. melt spinning) or is in contact with a crystalline substrate (e.g. a self-quenching process such as laser quenching), the nucleation process is no longer the controlling factor. Instead, the conditions

required for glass formation will be determined by either crystal growth kinetics and the related rate of crystal growth or the rate at which heat is removed from the interface region.

In analyzing crystal growth, Jackson (1958, 1967) notes that there are basically two types of interfaces, and indicates the entropy of fusion can be used to characterize them. Materials (such as iron) with small entropies of fusion ($\Delta S_m < 2R$) may be expected to have liquid-crystal interfaces which are rough on an atomic scale, while those with large entropies ($\Delta S_m > 4R$) are likely to have smooth interfaces.

The growth velocity (U_K) of an interface controlled by the kinetics of the system may, in general, be expressed as (Turnbull, 1962):

$$U_K = d v f \left| 1 - \exp \left| \frac{-\Delta G_c}{RT_i} \right| \right| \quad (9)$$

where d is the displacement necessary to locate an atom into a lattice position, T_i is the temperature at the interface and f is the fraction of preferred growth sites on the crystal-liquid interface (approximately unity for rough interfaces.) If the entropy of melting is temperature independent this may be rewritten as:

$$U_K = d v f \left| 1 - \exp \left| \left(\frac{-\Delta S_m}{R} \right) \left(\frac{1 - T_r}{T_r} \right) \right| \right| \quad (10)$$

For values of T_r between about 1.0 and 0.75, this may be linearized and written as:

$$U_K = d \nu f \left[\left(\frac{-\Delta S_m}{R} \right) \left(\frac{1 - T_r}{T_r} \right) \right] \quad (11)$$

Spaepen and Turnbull (1982) have indicated that for pure metals, ν is on the order of v_s/d , where, as a limiting case, v_s is the speed of sound in the material. However, in alloys which require solute redistribution (e.g. the Fe-B system), they report that ν may be estimated from the diffusivity (D) as:

$$\nu = \frac{6D}{d^2} \quad (12)$$

The value for $\Delta S_m/R$ in iron is approximately 1.0, thus growth interfaces are expected to be rough and f is taken as unity. Thus, for processes without compositional changes, the velocity of an interface can be written as

$$U_K = \left(\frac{6D}{d} \right) \left(\frac{\Delta T}{T_i} \right) \quad (13)$$

This expression represents the maximum velocity at which a solid-liquid interface can move and still allow the atomic rearrangements necessary to form the crystalline phase. Thus, in determining whether a material will solidify as a glass, this velocity must be compared with the interfacial velocity where the heat flux is the limiting factor controlling solidification. If the heat

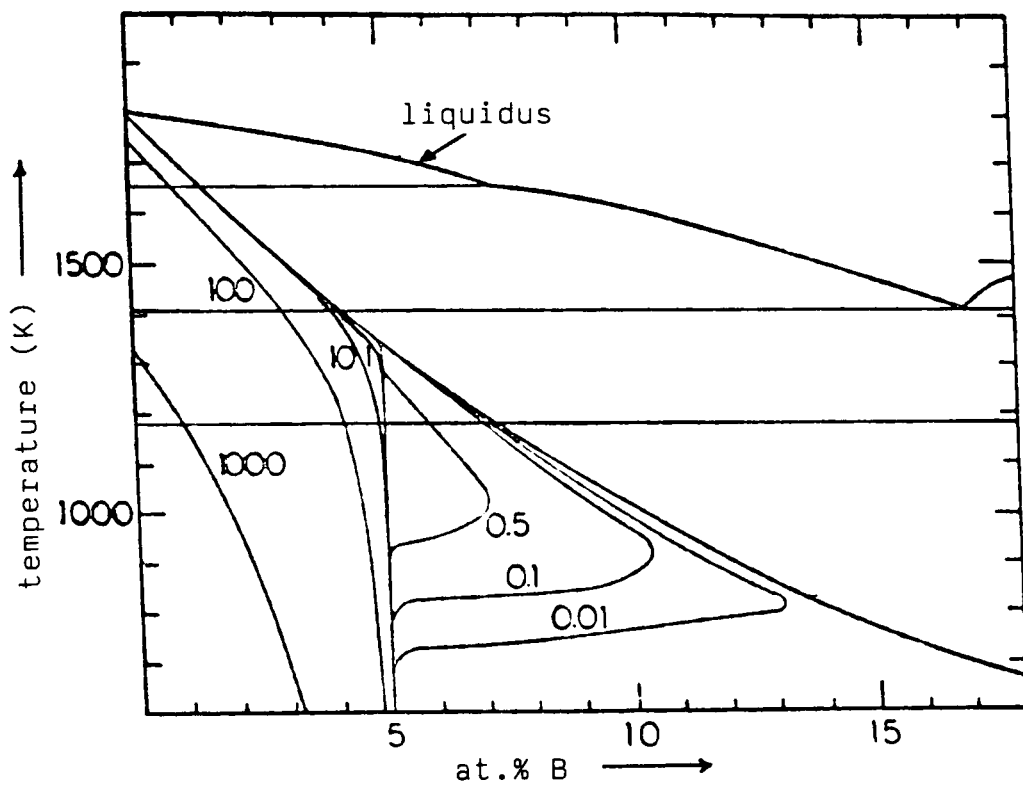


Figure 4. The Fe-B phase diagram with contours representing the bcc crystal growth velocity (in m s^{-1}) for the liquid $\rightarrow$ bcc transition as a function of composition and interface temperature. (Spaepen, 1985)

flux controlled velocity (U_h) is greater than U_k then solidification will take place without formation of the crystalline phase and the solid phase will be a glass.

This is the approach taken by Spaepen (1986) for the Fe-B alloy system where he computed the crystal growth rate as a function of boron concentration (Figure 4.) For a nanosecond laser with a melt depth of $1.4 \mu\text{m}$ and a solidification time of 70 ns, the thermally controlled interface velocity is expected to be about 20 m/s. The lower limit for amorphization, then, is expected to be about 4.8at%B.

CHAPTER II

THE IRON-BORON SYSTEM

The iron-boron system is one of the most widely studied TM-M glass forming systems. There are several possible reasons why this is so. First, this system requires only a moderate rate of cooling (about 10^6 K/s) for glass formation in the region of 15-20at% boron. Second, the amorphous alloy possesses electrical and mechanical properties which are superior to most other ferrous alloys. Lastly, both the methods of production which have been developed, as well as the materials themselves, makes the production of Fe-B glass relatively inexpensive. Thus, in addition to being an ideal material for research, this material has commercial potential as well.

Crystalline Phases

The phase diagram for the iron-rich portion of the Fe-B system is shown in Figure 5 and the lattice parameters for the stable and metastable phases are given in Table 1. Godbole (1986) investigated an Fe-20at%B alloy using x-ray diffraction and found that the equilibrium Fe_2B phase and ferrite are present following sinterization. Upon splat quenching, however, the diffraction pattern indicated the presence of the tetragonal metastable Fe_3B phase rather than Fe_2B .

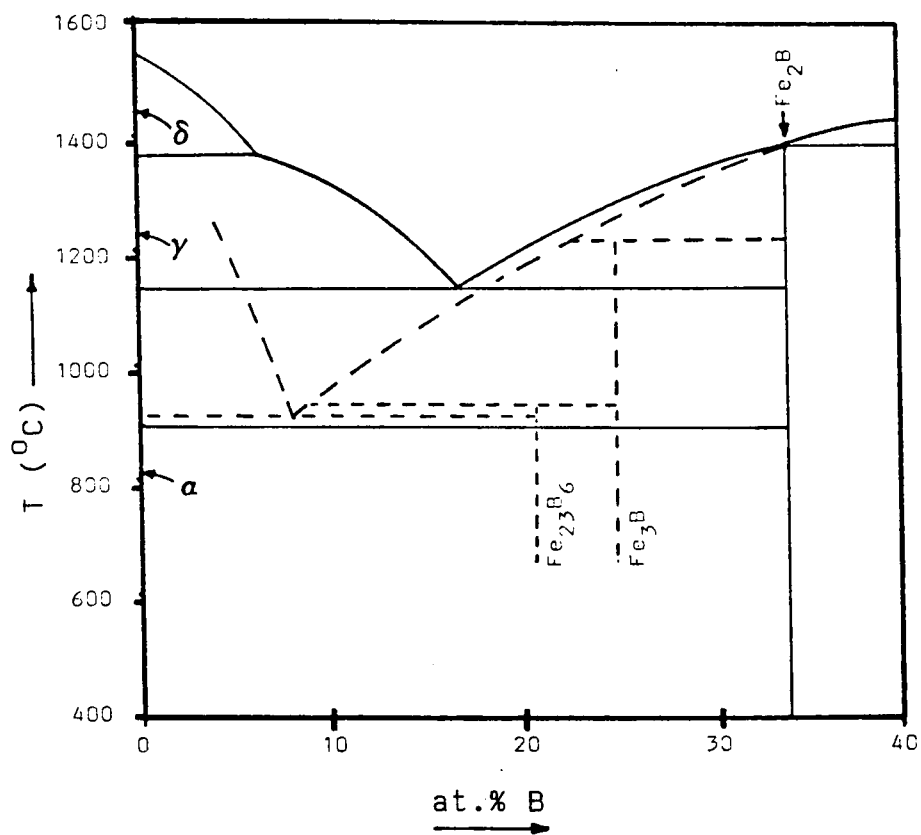


Figure 5. Phase diagram of the Fe-B system showing reported stable and metastable phases. (Herold and Koster, 1978)

TABLE 1 - Lattice Parameters of Phases in the Iron-Boron System (Herold and Koster, 1978)

Phase	Crystal Structure	Lattice Parameter (nm)
α -Fe	bcc	$a=0.287$
γ -Fe	fcc	$a=0.359$
Fe_2B	tetragonal	$a=0.511$ $b=0.428$
Fe_3B	tetragonal	$a=0.864$ $b=0.428$
Fe_3B	orthorhombic	$a=0.543$ $b=0.666$ $c=0.445$
Fe_{23}B_6	fcc	$a=1.067$

For Fe-B alloys with less than 12at%B, Ray and Hasegawa (1978) reported that rapid quenching (melt spinning in this case), can produce a metastable, body centered cubic, solid solution. Their evidence indicated that these solid solutions are substitutional, replacing, on the average, two iron atoms with three boron atoms while retaining the bcc structure. The lattice parameters for these solid solutions are shown in Figure 6.

Physical Properties

As is expected, the density of an amorphous Fe-B alloy is less than the stable, crystalline, two phase alloy of the same composition. However, the difference between the two is compositionally dependent, reaching a minimum at about 19at%B and increasing with departure from this composition (Figure 7.)

From a commercial point of view, the ferromagnetic behavior of the Fe-B glasses is perhaps one of its most appealing properties. Current power transformer technology relies on the Fe-3.2at%Si grain oriented alloy for construction of the transformer cores because of its low power loss characteristics. However, an amorphous Fe-20at%B alloy exhibits about half the loss of the Fe-Si alloy and it is estimated that if the transformers in use today were replaced with transformers with Fe-B cores, a savings of about \$250,000,000 per year would result.

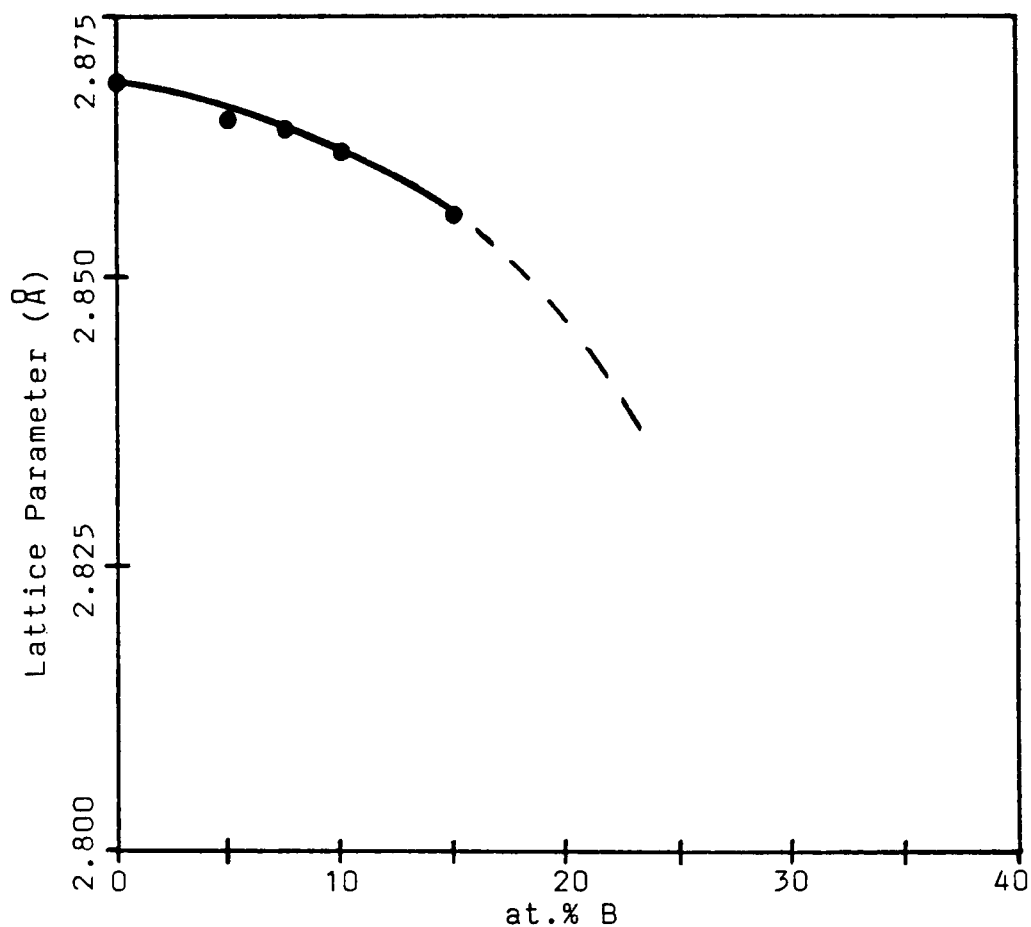


Figure 6. Lattice parameter of Fe-B solid solutions produced by melt spinning. Dashed line shows extrapolation of data by author. (Ray and Hasegawa, 1978)

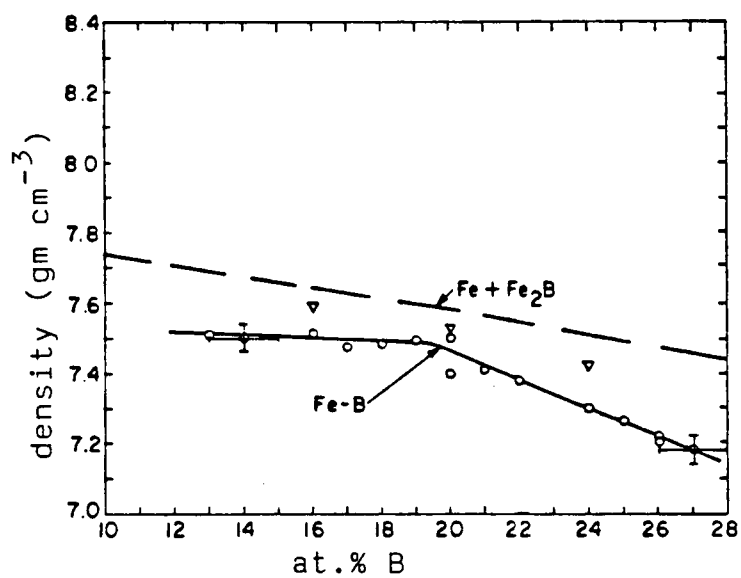


Figure 7. Density of Fe-B glass as a function of composition. The dashed line is for an equilibrium crystalline mixture of Fe and Fe₂B. (Ray, et al, 1977) ²

Mechanical Properties

The glasses formed in the Fe-B system have been found to exhibit exceptionally high strength and compressive (i.e. bending) ductility. The Fe-20at%B glass has an ultimate tensile strength of 65 GPa and a yield strength of 3.6 GPa. This compares well with other steels such as 18/8 CrNi stainless which has a tensile strength of 80 GPa and a yield strength of 0.6 GPa (Kunzi, 1983.)

The hardness is also extremely high and as is seen in Figure 8, has been found to increase with increasing boron content. When annealed, the hardness increases slightly with increasing temperature up to a critical temperature, at which point the sample undergoes crystallization and the hardness falls abruptly (Inal and Yost, 1981.) The temperature at which crystallization occurs is dependent on both the boron content and heating rate. Further, below about 17at%B, multiple crystallization points have been observed (see Figure 9.)

Structure of Glassy Fe-B Alloys

The electronic and atomic structures of glassy Fe-B alloys have been studied using a variety of techniques including x-ray and neutron diffraction, Mossbauer and Auger spectroscopy and x-ray photoemission spectroscopy (XPS).

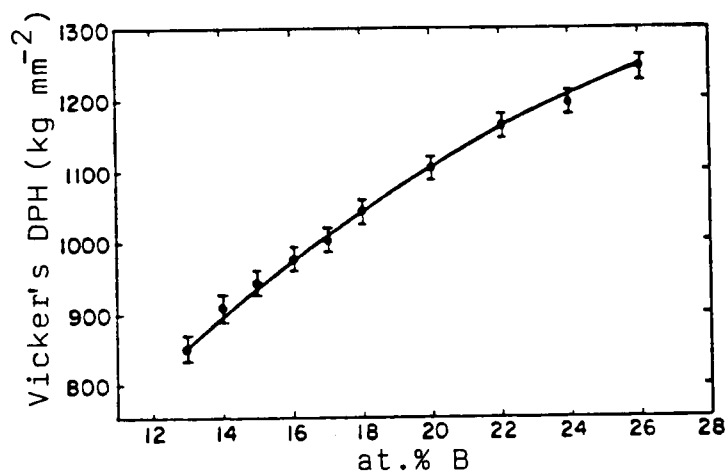


Figure 8. Vicker's diamond pyramid microhardness as a function of composition for Fe-B metallic glasses. (Ray, et al, 1977)

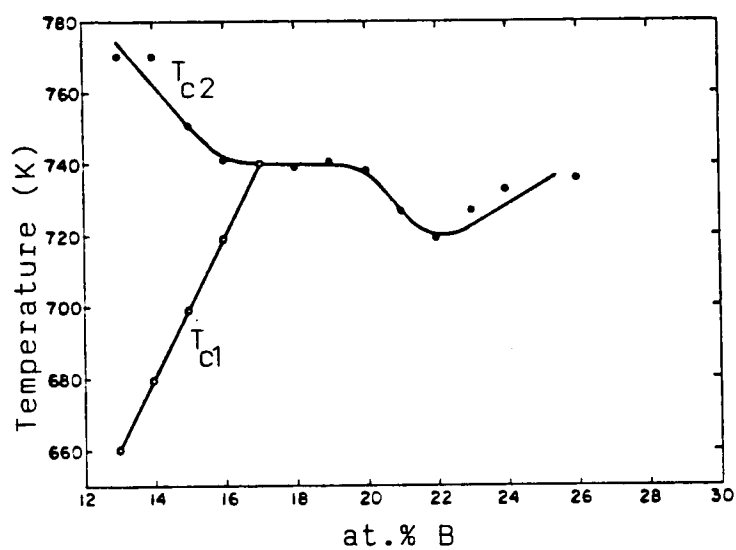


Figure 9. Crystallization temperature for Fe-B glasses, obtained at a heating rate of $20^{\circ}\text{C}/\text{min}$. (Ray, et al, 1977)

Naka et al (1976) reported that there was a correlation between the microhardness and the average electron concentration per metal atom in the Fe-dominated glassy alloys. Further, the strength of the metallic glasses was attributed to the bonding between the iron and the metalloid and that this bonding was changed and the strength diminished by TM alloy additions which result in an increased occupancy of the 3d band of the iron.

However, evidence by Hasegawa and Ray (1978) indicates that about 1.9 sp electrons per boron atom are transferred to the d band of iron. More recently, Mossbauer studies (Nakajima and Nagami, 1986), have shown that this transfer of electrons is not constant but increases with increasing boron content. Thus, the hardness of the alloy would be expected to decrease with increasing boron content; as shown above, this is not the case. Therefore, it seems clear that the nature of the iron-boron bond is changed with increasing boron content. XPS measurements by Matsuura, et al (1980) revealed additional energy of states on the lower energy side of the iron 3d band, which they attributed to the formation of covalent bonds between the iron 3d and boron 2p states. Further, a comparison of amorphous and crystalline Auger spectra as well as core and valence ELS spectra by Crescenzi, et al (1983) showed considerable difference between the electronic energy levels of the iron and

suggested a d-band filling closer to that of nickel for the amorphous alloy. Based on this, they interpreted the electronic properties within an FCC band theory. This is consistent with the observed increase in hardness with increasing boron content since there would be a tendency for the electrons donated by the boron to stabilize the local structure.

The coordination number for the Fe-Fe pairs from RDF data lends further support to this interpretation. In both amorphous as well as liquid Fe-B alloys (Mattern, et al, 1986; Nold, et al, 1983), the coordination number has been observed to be only slightly larger than that for an FCC material.

Numerous researchers (Mattern, et al; Nold, et al; and Hermann and Mattern) have analyzed RDF data from both liquid and amorphous Fe-B alloys and all concluded that the amorphous material is composed of micro-crystals. Further, Frahm and Pfalzgraf (1983) compared the RDF of liquid argon, liquid chlorine and noted that chemical bonding between nearest neighbors exists whenever the minimum following the first peak tends to zero. The RDF for amorphous Fe-20at%B shows such a minimum which implies chemical bonds between the iron atoms. This excludes "the description of the iron matrix as DRP based...and favors cluster models..." Thus, it would seem that the rejection

of the micro-crystal/cluster model in favor of the DRP model for the Fe-B system was premature.

CHAPTER III

LASER-METAL INTERACTION

Because they are clean, efficient, and economical, lasers are becoming widely accepted for use in industry. Current uses range from the welding and cutting of sheet and plate in heavy industry to repair of micro- and nanometer defects in integrated circuits. In all cases, however, their use centers around the ability to heat a precise spot on the workpiece. In most applications this heated region then cools rapidly by conduction when the laser is turned off. The cooling rates obtained in excimer laser experiments are in the range of 10^8 - 10^{12} K/s and often result in substantial modification in the structure of the irradiated material.

Coupling of Laser Energy With Metals

The major interaction of laser radiation with metals occurs when the conduction electrons in the metal are excited by the intense electromagnetic waves of the laser beam. The free electrons present in the conduction band are accelerated as a result of the absorption of energy from the field. Since the external field is changing, the kinetic energy is re-radiated (reflection.) For energy to be transferred to the lattice, the accelerated electrons must collide with the atoms of the crystal; the relaxation

time of this transfer is on the order of 10^{-12} s (White and Aziz, 1987.)

The degree to which coupling between the light and the metal occurs can be described by the reflectivity (R) which is related to the refractive index (n) by

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (14)$$

where k describes the attenuation of the electromagnetic waves across the material. For the higher frequencies the reflectivity is related to the plasma frequency of an electron gas in the metal and is high for light with a frequency lower than the plasma frequency. Figure 10 shows the normal spectral reflectance of solid iron for a number of different surface conditions. The reflectivity is seen to decrease rapidly below about 350 nm; thus, if the laser is chosen such that its wavelength is less than this, the coupling efficiency will be greatly increased. In metals, the liquid has a lower reflectivity than the solid and an increase in the coupling occurs when the metal melts. For an input energies greater than that required for melting, evaporation and plasma formation have been observed (Godbole; Walter, et al, 1981.)

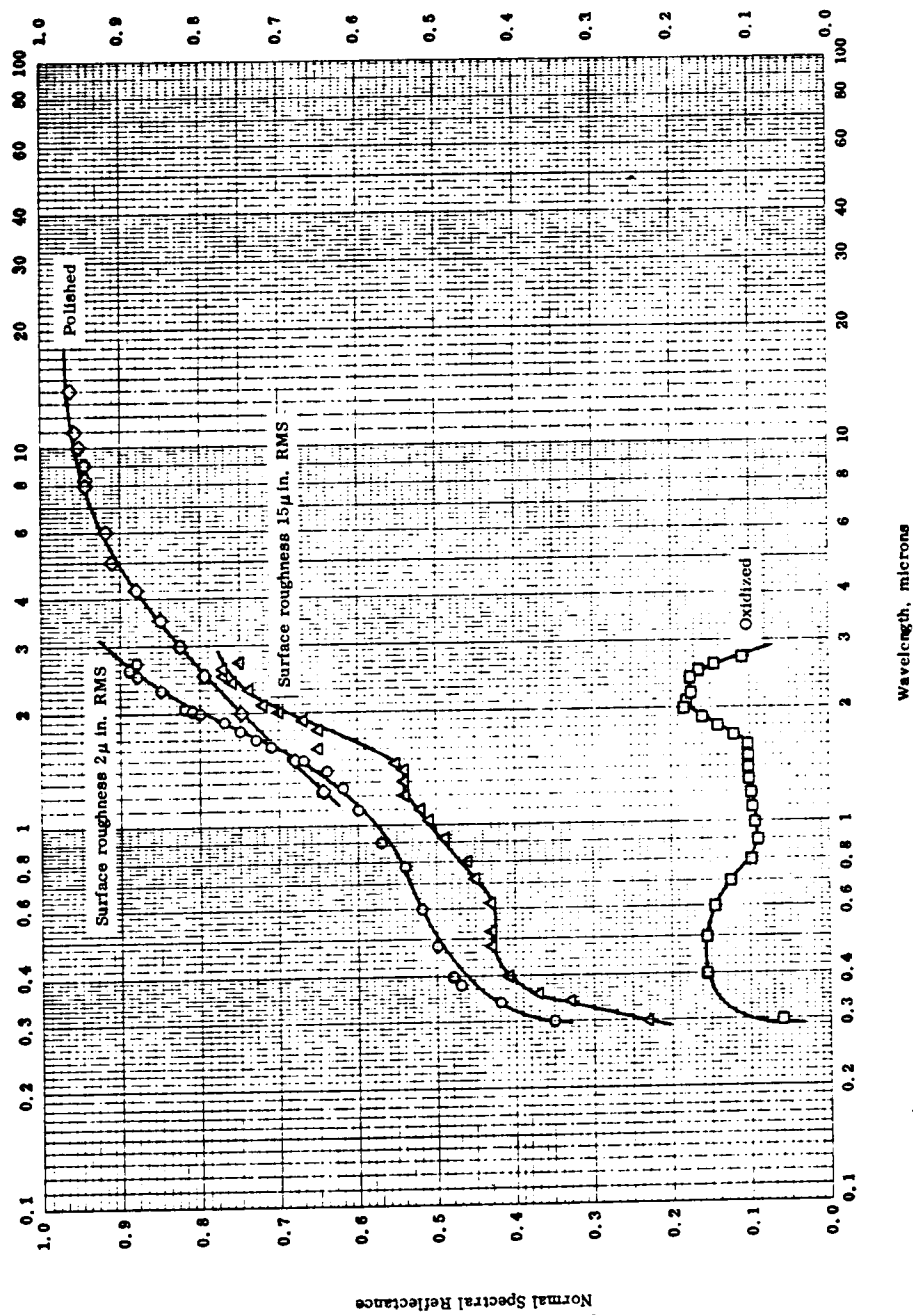


Figure 10. Normal spectral reflectance as a function of wavelength for pure iron. ("Thermophysical Properties of High Temperature Solid Materials", 1967)

Heat Generation and Temperature-Time Dependence

The change in power density as the light passes through a material can be written as

$$dI = -\alpha(x) I dx \quad (15)$$

where x is the penetration depth and α is the absorption coefficient. Integration gives the power density at x

$$I(x) = I_0 \exp \left[- \int_0^x \alpha(x') dx' \right] \quad (17)$$

where I_0 is the power density of the incident light. For metals, the absorption coefficient is on the order of about 10^6 cm^{-1} , thus the intensity decreases to e^{-1} after about 10 nm. Unlike the reflectivity, the absorption coefficient is nearly constant in the range of wavelengths of interest.

In a one dimensional approximation, the laser power density as a function of depth and time can be written as

$$(18)$$

Therefore, the power absorbed by the material in this layer is given by

$$I(x,t) = I_0(t) (1-R) [1 - e^{-\alpha x}] \quad (19)$$

This energy is readily transformed into heat. Using a random walk approximation, the average heat diffusion distance is estimated as

$$\Delta = \sqrt{2Dt_t} \quad (20)$$

For iron, the thermal diffusivity (D_{th}) is about $6 \times 10^{-2} \text{ cm}^2/\text{s}$ and letting t be the pulse duration (41 ns), we find that this distance is about 700 nm.

As discussed above, the heat is generated in a very thin layer (δ) near the surface, the thickness of which may be approximated by

$$\delta \approx \alpha^{-1} \quad (21)$$

Comparing this value with that of the heat diffusion distance shows that the laser interaction is, practically speaking, a surface heat source (i.e. $\delta \ll \Delta$). This has significant consequences for laser processing since small fluctuations in the beam power density will produce large variations in the temperature of the layer. These variations will cause certain regions to be completely evaporated, while others would exhibit little or no melting.

The dissipation of heat when materials are laser processed is primarily by conduction and to a lesser extent convection and radiation. Because of the large ratio between the diameter and depth of the melted region ($10^3:1$), the heat flow can be treated as a one-dimensional problem. While this simplifies the situation somewhat, no exact solution has been found, and numerical techniques are required to describe the temperature-time relation for the heating and cooling cycles (Mehrabian; et al, 1978; Hsu, et al, 1978.) Most of these assume no evaporation or plasma

shielding. Hassanein, et al (1984) included these effects in his work and, though the energy densities used in his calculations were two to three orders of a magnitude larger than those for excimer laser processing, he concluded that "vapor shielding has only a minor effect on the melt layer thickness..."

Godbole studied the melt depth as a function of incident energy density for pure iron for laser irradiation using a KrF excimer laser with a pulse duration at FWHM of 49 ns. Under these conditions he found that the melt depth tended to saturate above about 3.0 J/cm^2 (Figure 11.) He concluded an energy density of 3.0 J/cm^2 was an "appropriate choice in order to have considerable melt depth...with low surface damage."

Mixing in the Modified Region

It might be expected that the laser irradiated region is subjected to the usual mixing forces, namely convection and diffusion in the liquid and solid state diffusion following solidification. However, since the cooling rate using a nanosecond laser is so fast (10^{10} K/s), diffusion in the solid state can be assumed to be negligible. This is certainly the case, since amorphous materials prepared using cooling rates four orders a magnitude less than this (e.g. melt spinning) show no transformation to the crystalline phase during processing. The convective mixing case

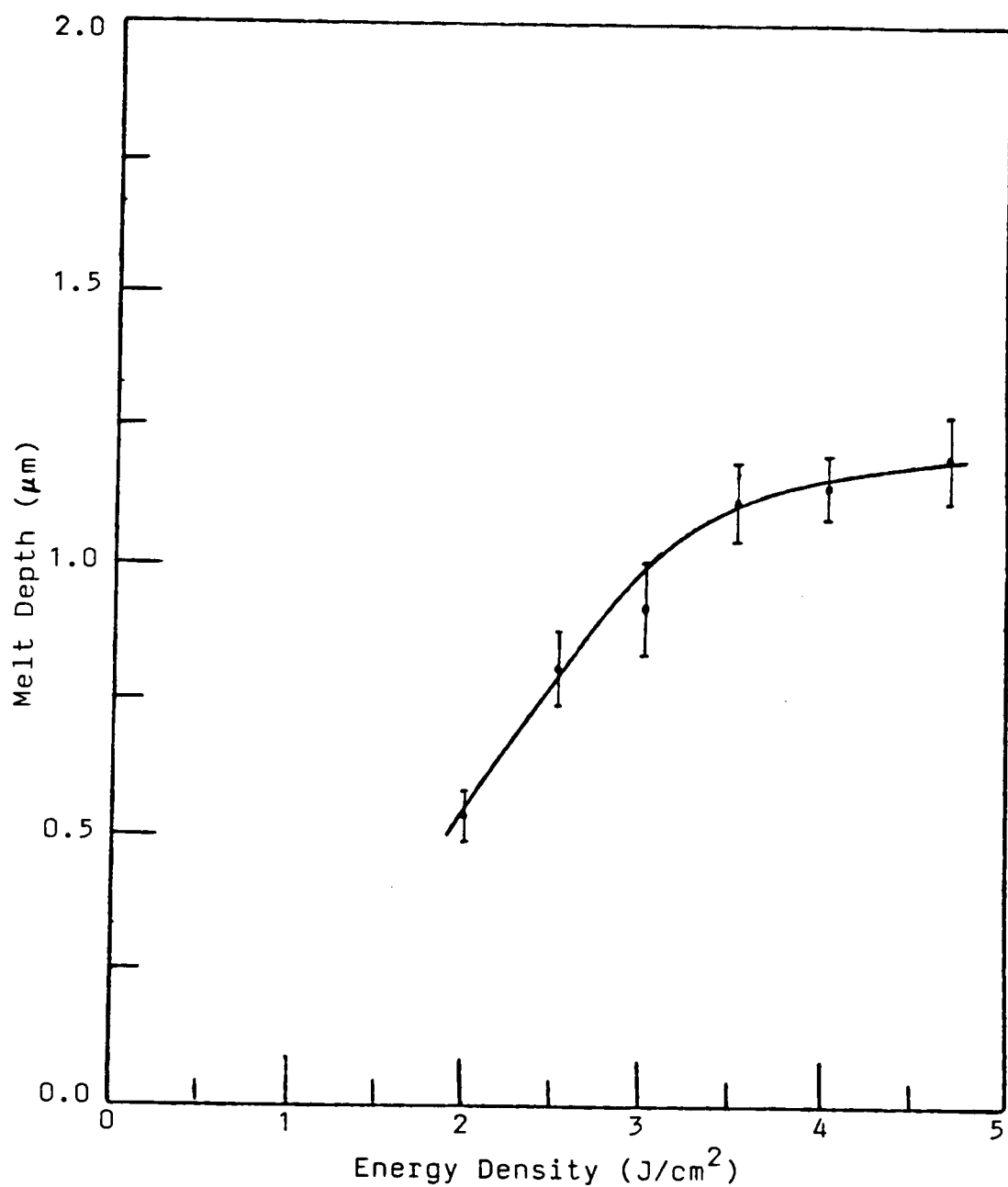


Figure 11. Melt depth of laser (KrF) irradiated pure iron as a function of energy density at the sample surface. (Godbole, 1986)

was studied by Possin, et al (1981) using a simplified model based on the Navier Stokes equation. With this model they determined that no convective mixing occurred when the fluid layer is much thinner than the spot diameter. Since the ratio of beam diameter to melt depth for excimer lasers is about $10^3:1$, convective mixing is also negligible. Thus, all mixing which occurs during excimer laser processing is due to diffusion in the liquid.

CHAPTER IV

EXPERIMENTAL PROCEDURE

Sample Preparation

An overview of the experimental procedure for this work is shown schematically in Figure 12.

Alloys of 5,10,15,20,25 and 30at%B were prepared from powders of iron (99.9% purity) and boron (99+% purity). After weighing, well ground mixtures were compacted in a hydraulic press into pellets of 10mm diameter and 10-12mm length. The pellets were then removed from the die, wrapped in tantalum foil and placed in a quartz tube. Zirconium turnings were added to the tube for gettering and the tube degassed and sealed under a 3×10^{-6} Torr vacuum. The pellets were sintered at 1423 K for 3 hours, and cut lengthwise for metallographic observation. The phases present in the sinterized samples were then analyzed with a Rigaku x-ray diffractometer in reflection mode.

Samples weighing between 0.04 and 0.3 grams were cut from the sintered material and prepared for splat quenching. A hammer and anvil apparatus was used for the splat quenching, and is shown schematically in Figure 13. The splat quenched sample was obtained by selecting a specimen with the appropriate weight and placing it on a copper anvil. The sample was then melted in a controlled

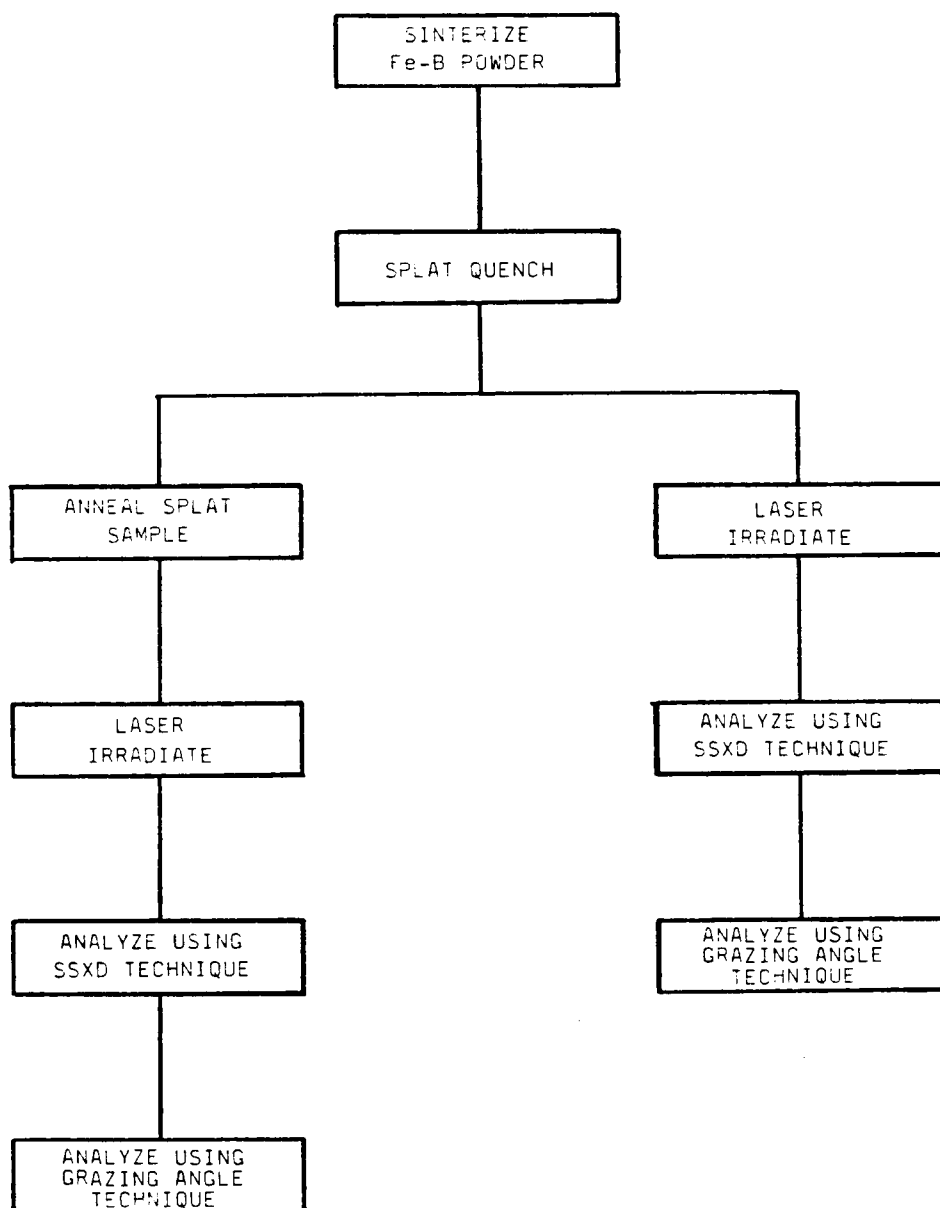


Figure 12. Schematic of experimental procedure.

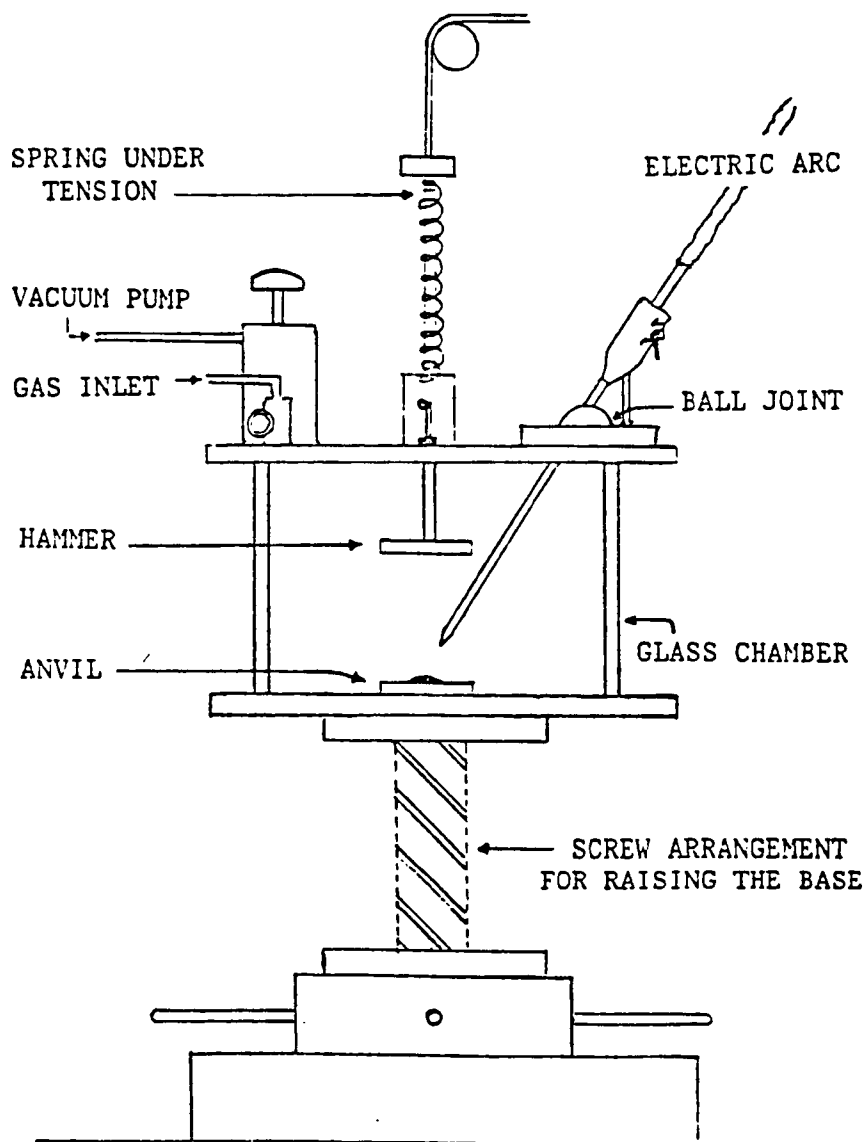


Figure 13. Hammer and anvil apparatus for splat quenching technique.
(Godbole, 1986)

atmosphere. When the sample had melted completely, the arc was removed and a spring-loaded copper hammer released. The hammer struck the molten sample on the anvil and the splat quenched specimen was produced. Each sample was analyzed by x-ray diffractometry immediately after quenching.

One set of samples was irradiated in the as-quenched condition, while a second set was annealed at 1025 K for 0.17-0.25 hours before the laser treatment. The samples were annealed by placing them in a quartz tube which was evacuated to 10^{-3} Torr, flushing with argon three times and then performing the anneal under a vacuum which was better than 10^{-3} Torr. Immediately after being annealed, each sample was again analyzed by x-ray diffractometry. Finally, a series of 20at%B samples was used in the as-quenched condition to study the glass forming ability of a known glass former under different laser energy densities.

Excimer laser experiments were then carried out at the Oak Ridge National Laboratory (ORNL) Solid State Division. A XeCl excimer laser with a wavelength of 308 nm and a full width at half maximum (FWHM) pulse duration of 41 ns was used in this study. For calibrating the output energy density the laser was equipped with a calorimeter which was able to measure the output energy density up to $4.5\text{J}/\text{cm}^2$. The desired energy density was obtained using the optical system shown schematically in Figure 14. This

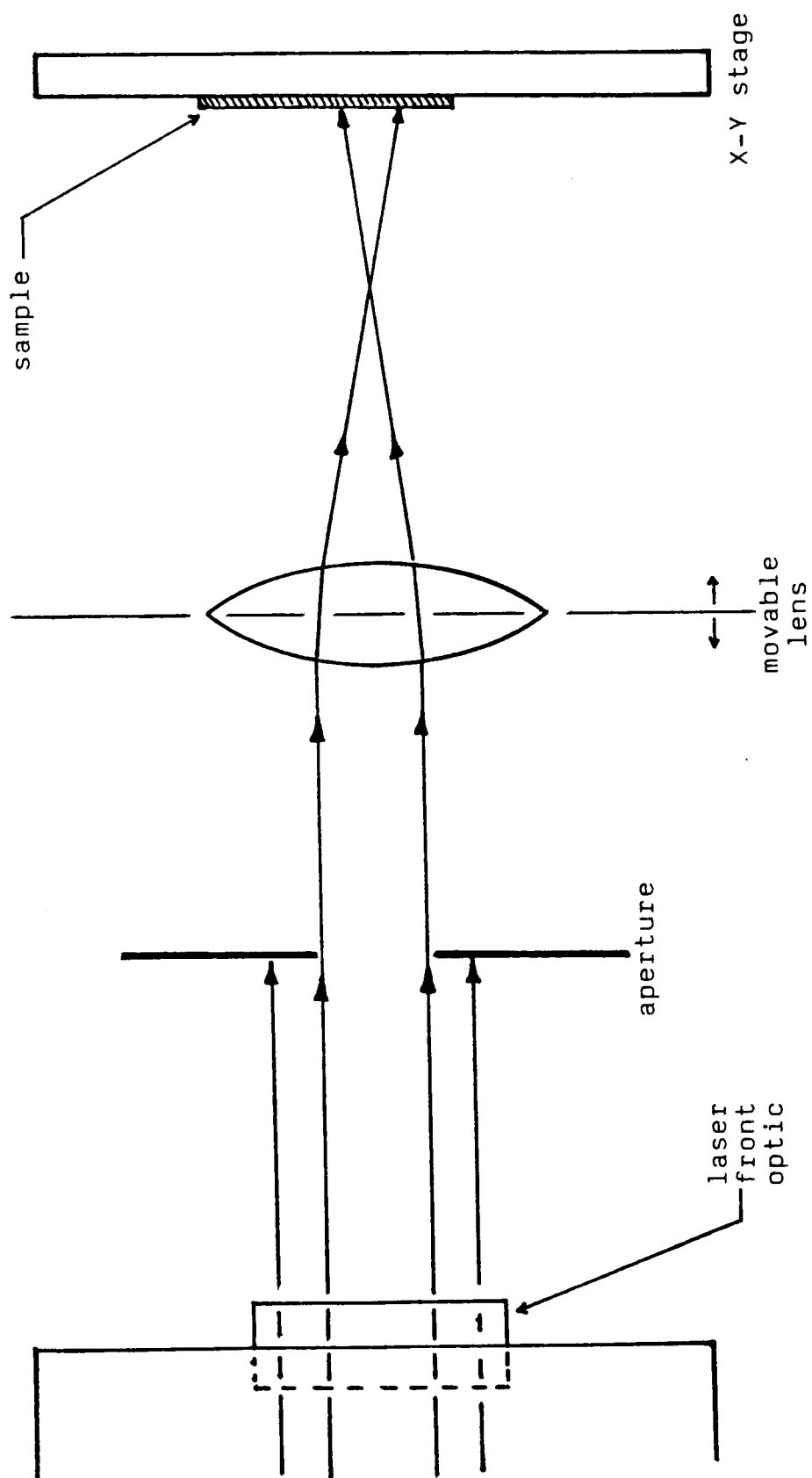


Figure 14. A schematic diagram of the optical system used to obtain a range of energy densities at the sample surface.

was done by inserting the calorimeter between the rectangular aperture and the lens used for focussing the beam. Once the beam energy was known, the required energy density was obtained by moving the focussing lens so that the beam would be focussed on a smaller area. Recalibration to compensate for the degradation of the active gasses in the laser cavity were made 3 times every hour or more often if necessary. This calibration was done by checking the instantaneous beam intensity and then making the necessary adjustment to the lens. Following laser processing, the samples were again analyzed by x-ray diffractometry.

The Rigaku diffractometer system used during this work is interfaced with a Digital Equipment PDP 11/34 computer with software for qualitative and quantitative analysis. The diffractometer system has its own micro-processor which may be programmed independently of the PDP 11/34. The conditions which may be programmed include the option to perform a step or continuous scan, the axis of rotation, number of repeat scans, starting and finishing angles, scan speed and the time constant. The peak information may be stored in the computer or recorded on chart paper. In addition, a hot stage is available which may be used to study the thermal stability of the materials. The x-ray source is a water cooled copper target which was operated at 35kV and 20mA.

The Bragg angles for phase determination were computed for each of the phases in Table 1 and are given in Appendix A. Integrated intensities before and after laser quenching were computed for the predominant reflections (110), (200), (220), (211) and (310) of α -iron (Figure 15.) The integrated intensity of the reflections was measured by scanning a region of about 3° around the diffraction maximum. To reduce the statistical error three scans of each line were taken and the diffracted intensity obtained by subtracting the background values from the measured total intensity. The background was determined by counting in each border of the corresponding region half of the total time employed in the scan and adding the results of the two measurements. The effect of laser processing was determined by comparing the integrated values obtained before and after laser quenching using the surface sensitive x-ray diffraction (SSXD) technique described in Appendix B.

A pure iron standard was scanned at the beginning of every series of runs and again every 4-6 hours thereafter. Furthermore, it had been observed that a stable target temperature was a prerequisite for a stable x-ray beam, therefore, no samples were scanned before a one hour equipment warmup period was completed.

Several of the sintered samples were polished and etched with Nital and Picral for metallographic observation.

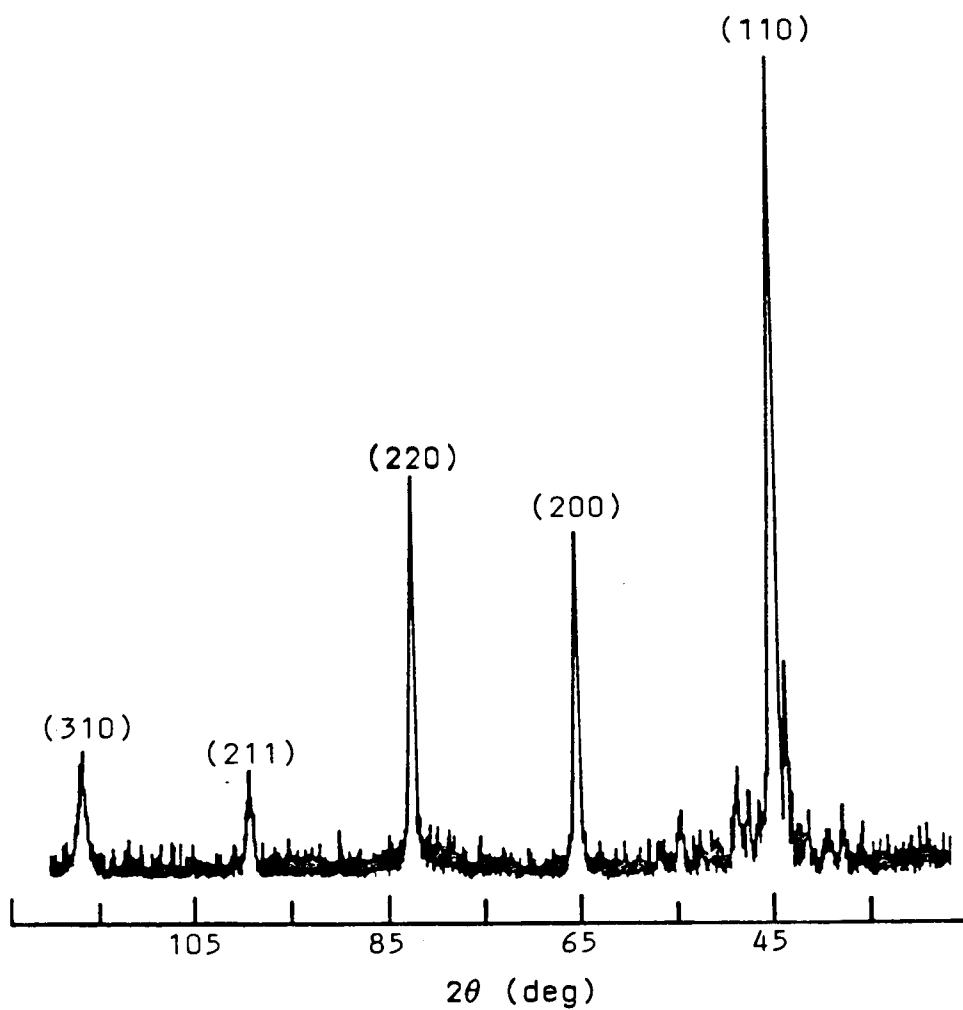


Figure 15. Diffraction pattern of an as-quenched Fe-20at%B sample showing the predominant α -iron reflections.

It was observed that with Nital the α -iron etched at a much higher rate than the borides. Specimens for scanning electron microscopy were electropolished and etched. The electropolishing solution consisted of 90% glacial acetic acid and 10% perchloric acid at 5°C with a current of 45mA.

Microstructural examination up to 20,000X magnification was done with an AMR-900 Scanning Electron Microscope (SEM) at the University of Tennessee. For higher magnifications a JEOL-840 SEM at the Oak Ridge Gaseous Diffusion (K25) Plant was used.

X-ray Analytical Techniques

A method for detecting and precisely measuring the thickness of a near surface layer in which massive structural changes (e.g. amorphization) had occurred was developed. This technique uses x-ray diffractometry in parafocusing geometry and has been applied to laser processed Fe-20at%B and Fe-Zr materials (Godbole) and was described previously by us (McCamy, Godbole, Lowndes, and Pedraza, 1986).

This surface sensitive x-ray diffraction (SSXD) technique requires that at least 60% of the diffracted intensity come from the modified layer if the measurement of the thickness is to be accurate. Further, it is essential that part of the beam penetrate the unaffected substrate material. Thus, the x-ray source selection for

performing the measurements will depend on the absorption coefficient of the specimen and the thickness of the modified layer. When measuring thin layers it is necessary that the x-rays emitted be strongly absorbed by the sample material. To meet this requirement, the wavelength of the target K_{α} radiation must be slightly shorter than the absorption-edge wavelength of the elements of the specimen. For instance, the K edge wavelength of iron is 0.1743 nm; therefore, either nickel ($\lambda_{K_{\alpha}} = 0.166$ nm) or copper ($\lambda_{K_{\alpha}} = 0.154$ nm) could be used as target elements (International Tables for x-ray Crystallography, 1974.)

The parafofocusing geometry used in the SSXD method is shown schematically in Figure 16. For a specimen in this arrangement the thickness (δ) of a modified layer when it contains no crystalline material is given by:

$$\delta = \frac{\sin \theta_i}{2\mu'} \ln R_i^{-1} \quad (22)$$

Where R_i is the ratio of the intensity of the diffracted peak at θ_i before and after the layer has been formed and μ' is the linear absorption coefficient of the modified layer.

For the case where the modified layer contains a volume fraction ν of crystalline material, the following system of equations may be solved to give an implicit equation for ν ,

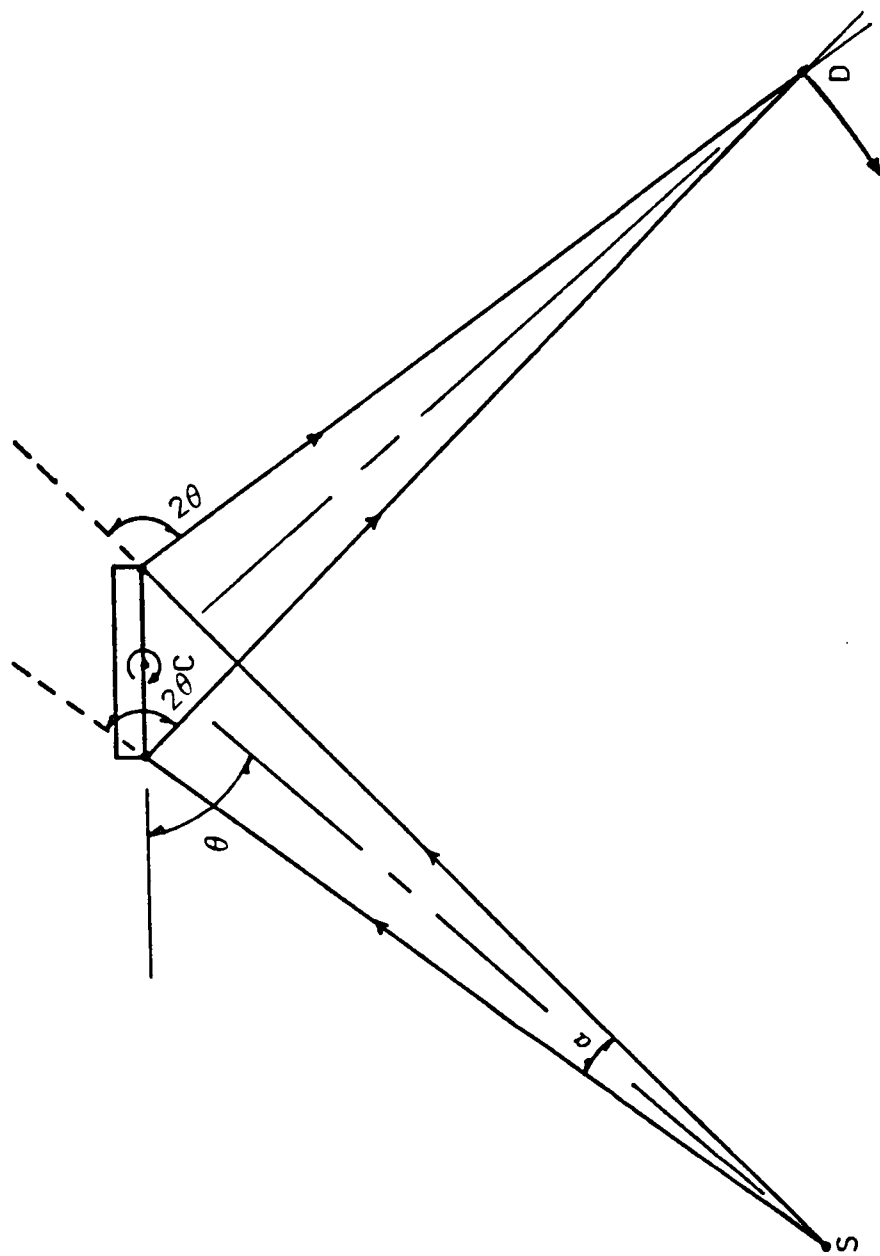


Figure 16. Schematic of parafofocussing diffraction geometry. S is the x-ray source, D is the detector which moves on an arc with constant radius CD , and C is the center of rotation for the sample and is located at the vertical centerline of the surface of the sample. The rotation velocity of the sample is $1/2$ that of the detector so the θ - 2θ relationship is maintained.

$$R_2 - \nu' = (R_1 - \nu')^{n_{12}} (1 - \nu')^{1 - n_{12}} \quad (23)$$

where

$$n_{12} = \frac{\sin \Theta_1}{\sin \Theta_2} \quad (24)$$

and the indexes 1,2 refer to any two peaks. Once ν is known, the thickness can then be obtained from

$$\delta = \frac{\sin \Theta_i}{2\mu'} \ln \left(\frac{1 - \nu'}{R_i - \nu'} \right) \quad (25)$$

The development of this technique and the derivation of the relations given above can be found in Appendix B.

For the iron-based samples and copper x-ray target used in this study, the upper limit of thickness detection is 2-4 μm as imposed by the maximum penetration depth of the x-rays. On the other hand, the lower detection limit is dependent on the ratio of peak-to-background intensities. As is well known, the probable error in the integrated intensities is proportional to $N^{-1/2}$, where N is the number of counts. The method used for calculating the error is given by Klug and Alexander (1974) and is based on the total number of counts and the ratio of peak-to-background intensities. Figure 17 shows the number of counts required to give a desired degree of accuracy for various peak-to-background ratios. This ratio was about 10 for the α -iron peaks for a probable error of about 1%.

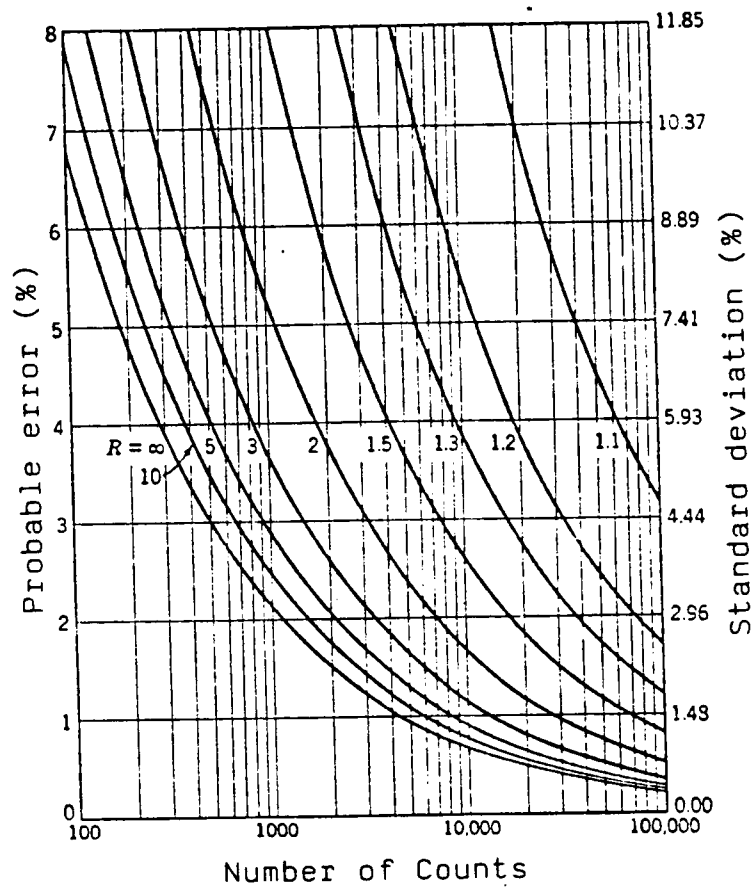


Figure 17. Number of counts required to give a desired degree of accuracy for various ratios of total to background rate. (Klug and Alexander, 1974)

Thus, a scan time for each peak was chosen to give a total count of about 10,000.

Figure 18 is a plot of amorphized layer thickness vs. the intensity ratio for the different peaks analyzed using the assumption that $\nu=0$ and $r_i=1$. From this plot it is seen that the lower detection limit is 50 nm if the (110) and (200) peaks are used. However, because the ratio for the (200) peak is about 0.93, with the background counted in our experiments the probable error is about 70%. Further, for situations where r_i approaches 1, the probable error can increase significantly. A complete evaluation of the accuracy of the SSXD method as it applies to this work is given in the following chapter.

The SSXD technique in parafofocusing geometry allows us to determine the volume fraction of crystalline material in the modified layer, but it only provides us with limited information as to the location of this material. Therefore, a non-parafofocussing geometry diffraction technique was employed in order to provide more information about the crystalline material in that layer. In the parafofocussing geometry, for very thin layers, the path length through the modified layer is so small, that only a small fraction of the diffracted beam comes from that layer. If the beam path is altered so that more of the beam is diffracted from the modified region relative to that from the substrate, much more information about that layer can be obtained.

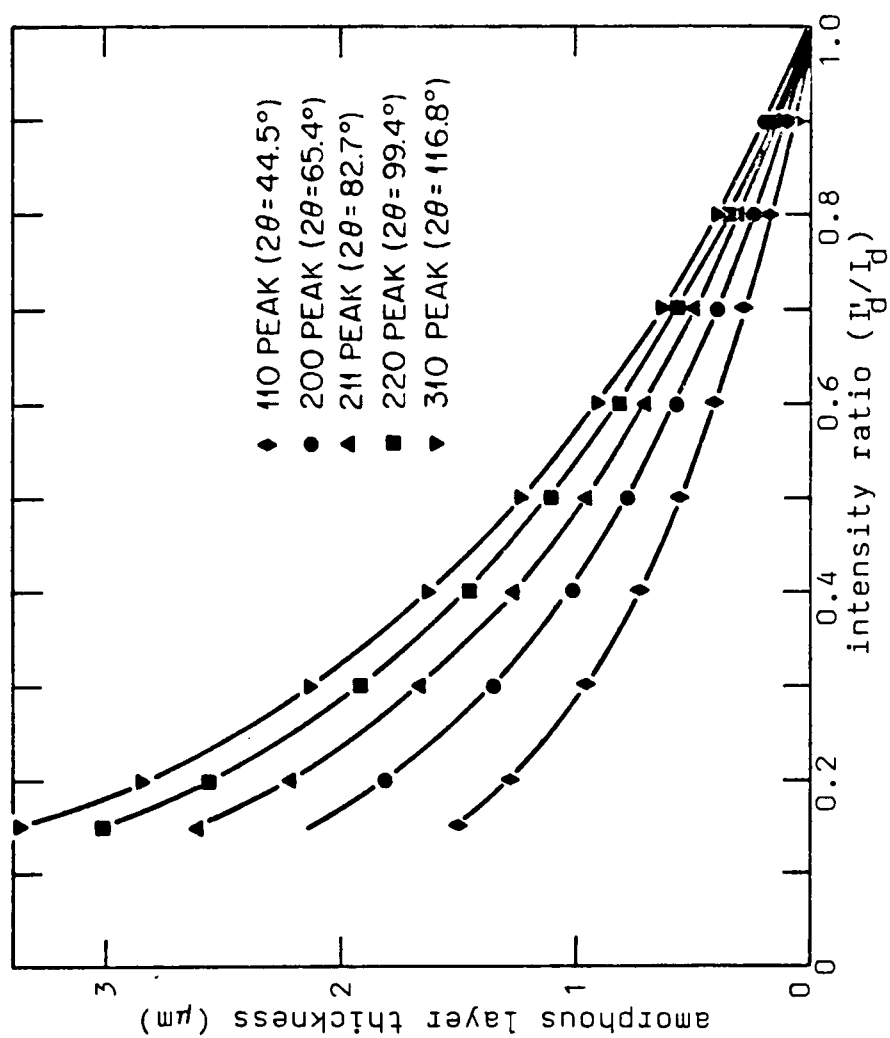


Figure 18. Amorphous layer thickness (in μm) versus x-ray intensity ratio for an Fe-B alloy with 0% crystalline volume in the amorphous layer.

The beam path through the sample for the grazing angle technique is shown in Figure 19; as can be seen, for smaller incident angles, the beam path through the layer is increased and the depth being probed is decreased. In this geometry, the path through the thin film increases as $(\tan \beta)^{-1}$. Thus, by scanning the sample at various incident angles, a profile of the modified layer may be obtained.

Because the grazing angle method relies on both the absorption of the sample as well as the ability to alter the geometry parameters, it was chosen as a complementary technique.

In the non-parafofocusing geometry used, only a small portion of the parallel beam is received by the detector, making accurate, quantitative measurements difficult. A thin film detector (TFD) is required to overcome this limitation; however, since a TFD was not available, only the distribution of the crystalline material within the layer could be studied.

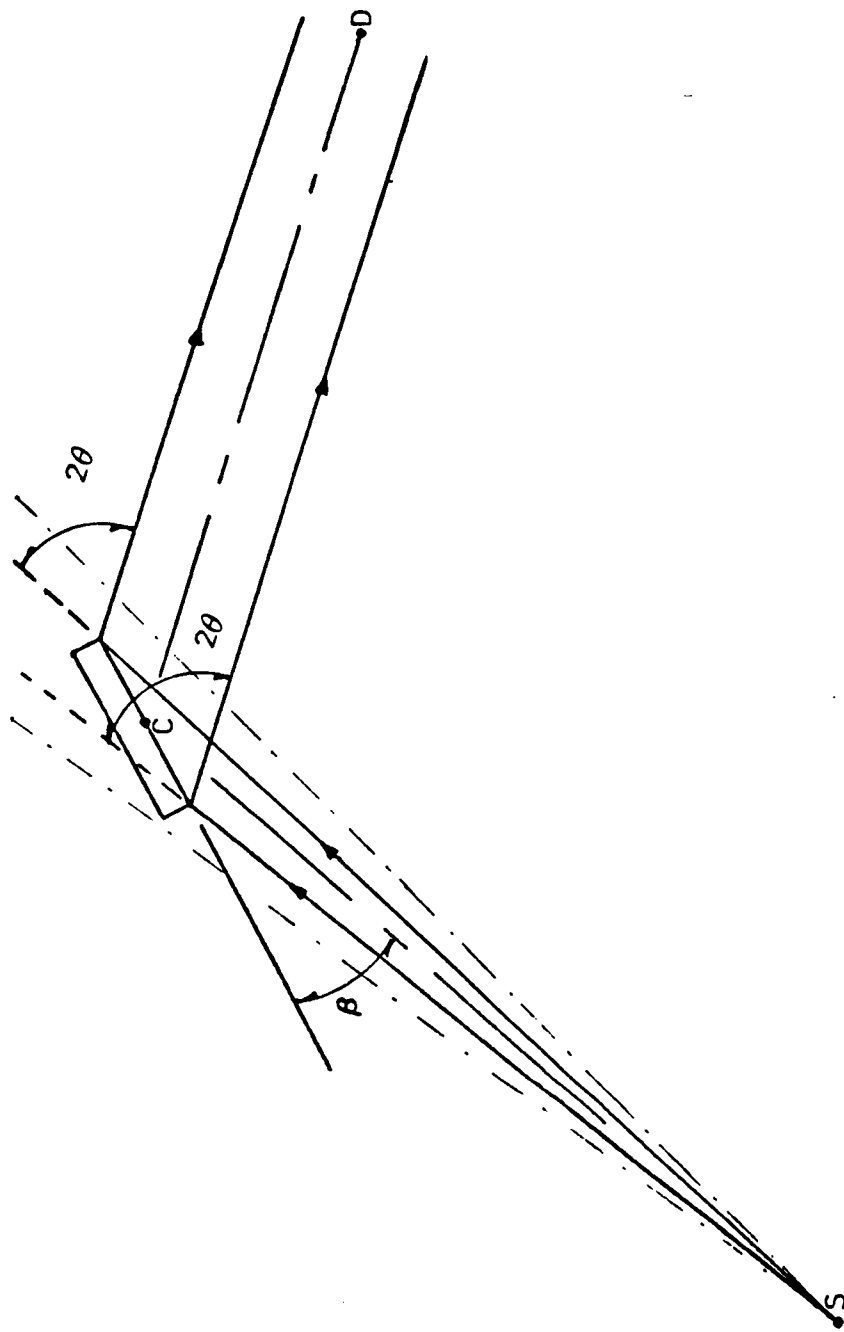


Figure 19. Grazing angle diffraction geometry. S is the x-ray source, the detector is located at D and C is the vertical centerline on the surface of the stationary sample. The source location and 2θ angles are the same as those in Figure 16, however, because of the geometry, the diffracted beams are practically parallel. The grazing angle β is fixed and held constant throughout the run.

CHAPTER V

EXPERIMENTAL RESULTS

Evaluation of the SSXD Technique

The accuracy of the SSXD technique was evaluated by independent measurement of the amorphous layer thickness on an Fe-20at%B specimen using SEM (McCamy, Godbole, Pedraza and Lowndes, 1986.) The specimen was irradiated with a laser energy density of 3 J/cm^2 . Earlier work (Godbole) had shown that for this fluence the layer is typically 1-2 μm thick. Thus it was expected that the layer thickness measurement would be quite accurate.

Figure 20 shows a micrograph of a transverse section of the irradiated sample, where the amorphous layer can be clearly observed. A 2.02 μm latex sphere, used for calibration purposes, is also shown. Some variation in the thickness of the layer is observed in the micrograph, with a minimum thickness of 1.15 μm and a maximum of 1.25 μm , the average being 1.2 μm . This measurement is slightly less than the value $1.3 \pm 0.1 \mu\text{m}$ obtained by the SSXD method.

Two main reasons may account for the small difference in the mean values. First, it is clear that the value from the SSXD method is an average over the incident area of the x-ray beam and the transversal section analyzed with SEM may be slightly off this average. Second, since the x-ray

Cu Plating

2.02 μm
Latex
Sphere

Amorphous
Film

Fe-20at%B
substrate

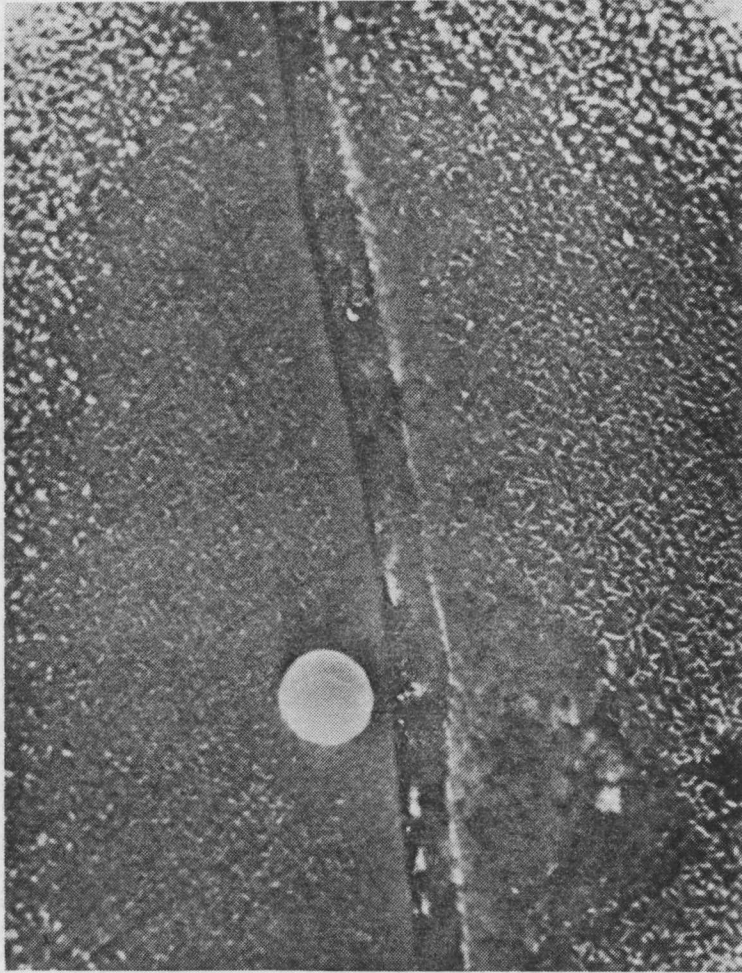


Figure 20. SEM micrograph of a transversal section of a laser processed Fe-20at%B sample. The amorphous layer is observed between the copper plating and the substrate.

radiation used is about 0.02 nm (1.3KeV) from the absorption edge of the iron, the value of the absorption coefficient may have an error approaching 5%. This effect would enlarge the error bar by about the same amount since the linear absorption coefficient (μ) is simply a multiplicative constant in the formulas.

Sintered Material

The sintered iron alloys were mounted on a suitable holder and x-ray patterns obtained by a continuous $2\theta/\theta$ scanning method. Analysis of the diffraction peaks indicated the equilibrium phase Fe_2B was present together with α -iron in all the samples.

The alloy containing 30at%B was too hard and brittle to be cut and x-ray analysis of the sintered alloy was not possible. However, based on the results of the other alloys and the as-quenched 30at%B alloy, it is reasonable to assume that the Fe_2B and α -iron phases were present in this material as well.

As-Quenched Material

Characterization of As-Quenched Material

Pieces of the sintered material were cut and splat quenched using the hammer and anvil technique described earlier. The sample weights were typically in the range of 0.08-0.30 grams. For the alloy containing 20at%B, however,

sample weights as low as 0.04 grams were used. The quenched thin foil samples were analyzed by x-ray diffraction. Figure 21 shows the diffracted intensity vs. the angle 2θ for an as-quenched Fe-20at%B alloy. In samples with less than 30at%B and weighing more than about 0.08 grams, a mixture of the tetragonal Fe_3B metastable phase and α -iron formed during quenching.

For the 5at%B samples the α -iron lattice constant was determined to be 0.28655nm. This value is consistent with that given by Ray and Hasegawa (1978) for a solid solution of iron containing about 2.5at%B.

In the case of the 20at%B, 0.04 gram alloy (Figure 22) not only were the diffraction peaks for the α -iron and Fe_3B phases observed, but also a "hump" centered about the (110) peak of the α -iron which is characteristic of the amorphous Fe-B phase. Thus, it was found that the phases present in the as-quenched samples could be controlled by changing the sample weight.

Analysis of the diffraction pattern of an as-quenched 30at%B sample indicated that this material retained the equilibrium Fe_2B phase during quenching.

Laser Treatments of As-Quenched Material

The as-quenched alloys were then irradiated with the pulsed XeCl laser by scanning over their entire surface area. The energy density of the laser beam was maintained

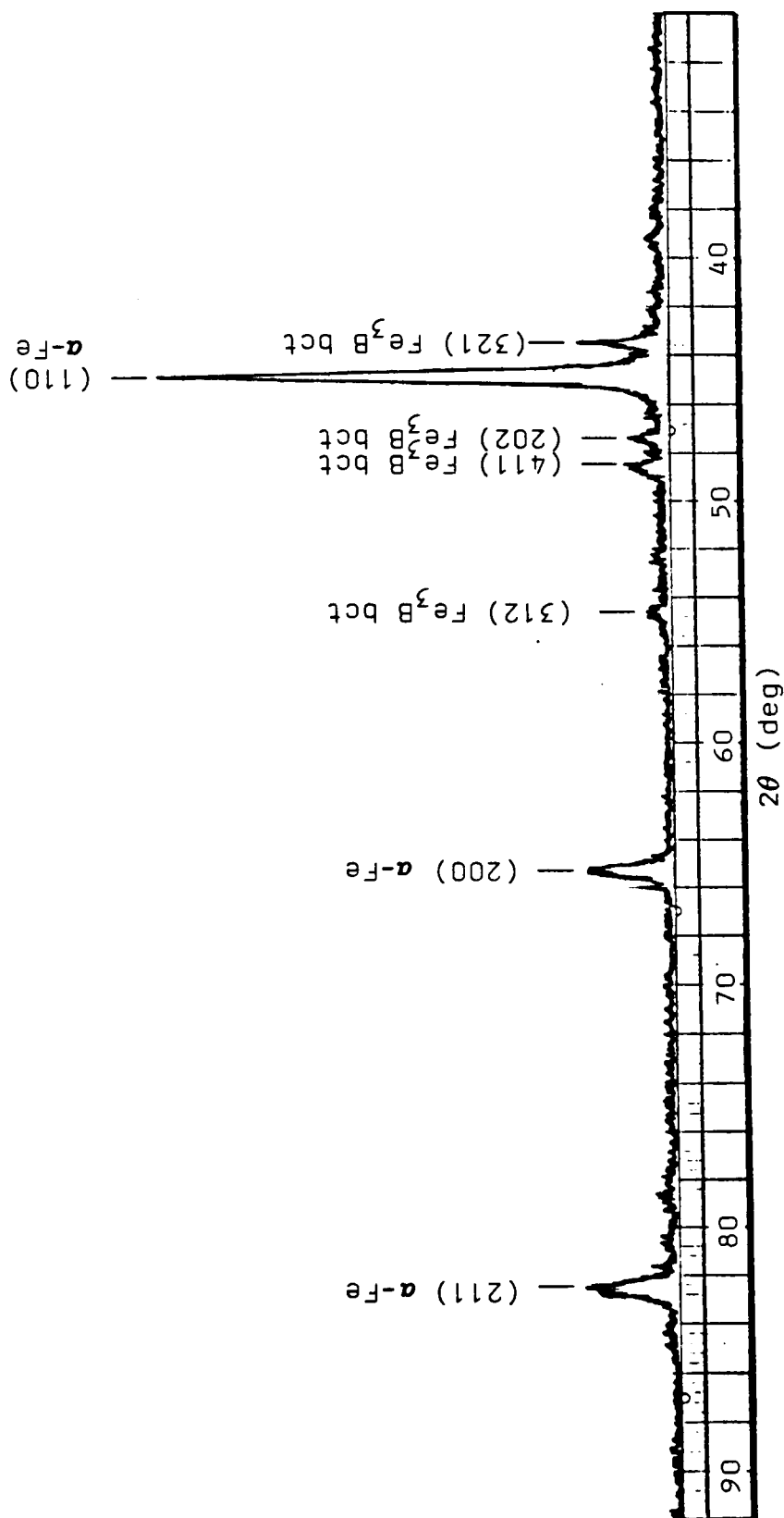


Figure 21. X-ray diffraction pattern of an as-quenched Fe-20at%B alloy prior to laser processing.

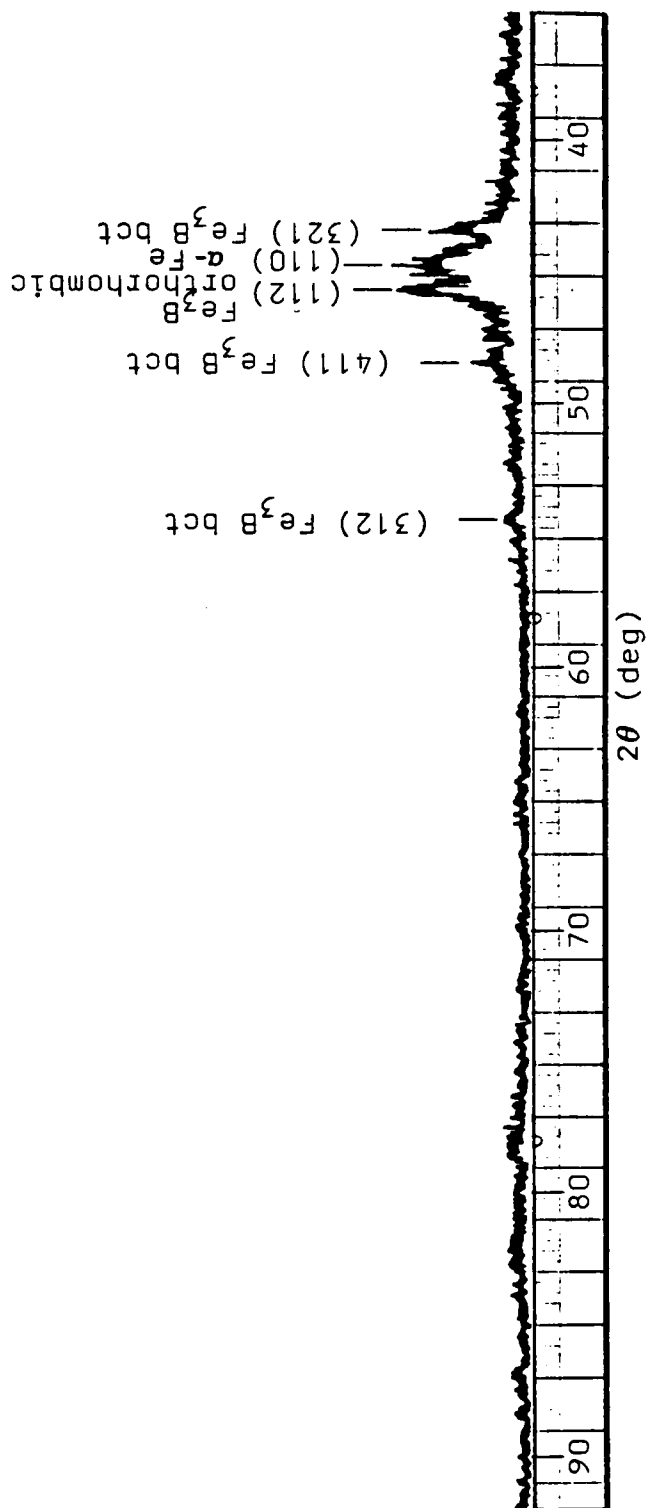


Figure 22. X-ray diffraction pattern of an as-quenched 0.04g Fe-20at%B sample. The presence of the 'hump' between 40-50° indicates the sample is amorphous.

at 3.0 J/cm^2 . Post-irradiation diffraction patterns were then obtained. Amorphization was observed to have occurred in greater or lesser degrees in all the samples except those containing 5at%B.

None of the 5at%B samples showed any evidence of amorphization in the post-irradiation pattern (Figure 23), however, second set of peaks was observed. This second set of peaks, shown in more detail in Figure 24, was indexed as bcc and the lattice constant was determined to be 0.2840 nm. This value is 0.93% less than that of pure iron and 0.90% less than that of the iron-boron solid solution found in the original splat quenched material. X-ray diffraction scans made using the grazing angle technique showed that the intensity of the peaks belonging to this second (α') phase did not decrease as quickly as those belonging to the α -iron when the grazing angle (β) was decreased. Further, no change in the lattice constant of the α -iron was observed following irradiation. This indicates that the modified layer was composed predominately of the α' phase, while the substrate is composed of α -iron with 2.5at%B in solid solution.

The diffraction pattern for the 10at%B sample (Figure 25) indicated that both the α' phase and amorphous Fe-B is formed when this material is irradiated. Analysis using the SSXD method indicated that the volume fraction (ν') of crystalline material in the layer was about 30% for one

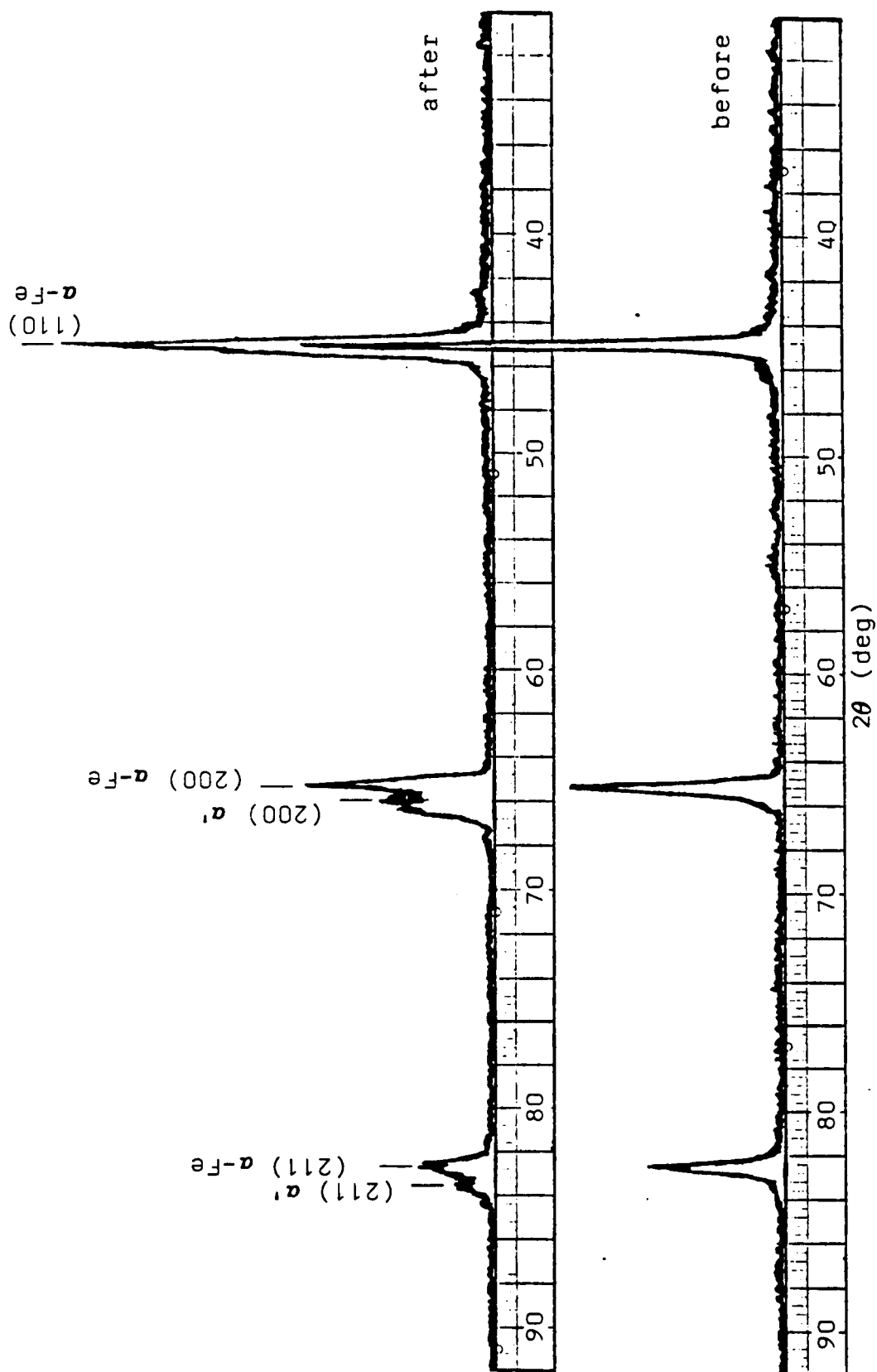


Figure 23. X-ray diffraction pattern of as-quenched Fe-5at%B sample before and after laser processing.

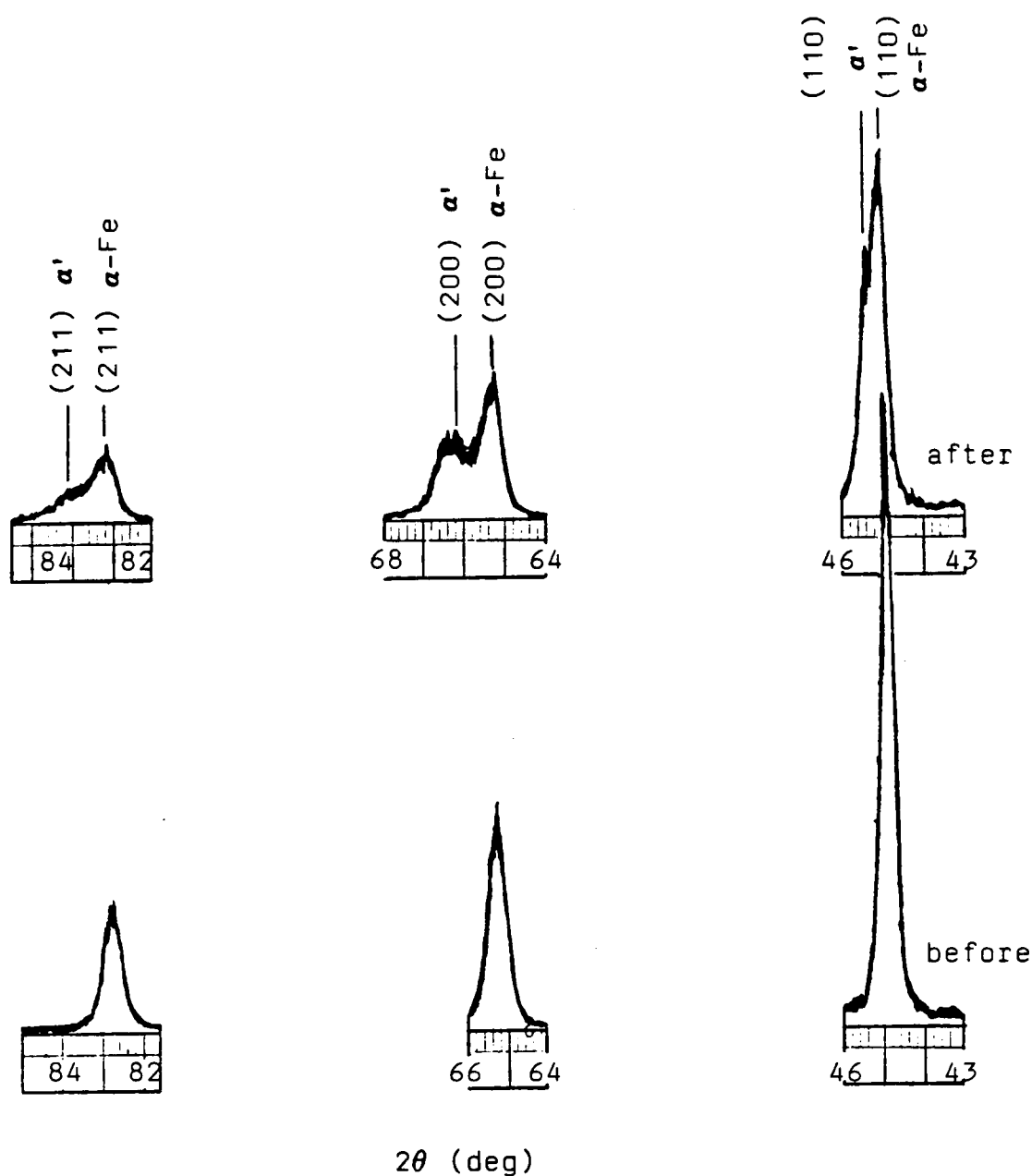


Figure 24. X-ray diffraction pattern of an as-quenched Fe-5at%B sample before and after laser processing showing detail of the α -iron and α' peaks.

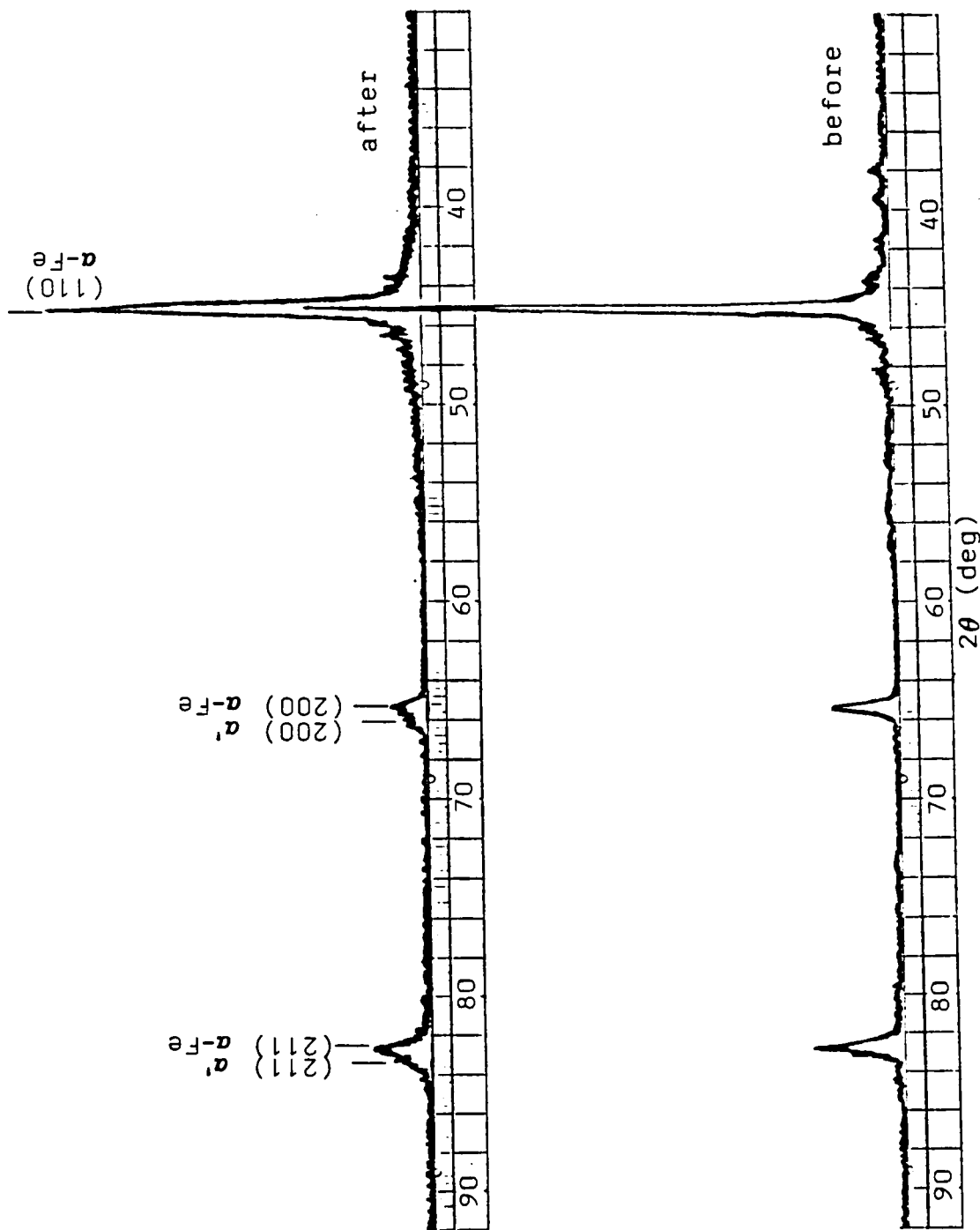


Figure 25. X-ray diffraction pattern of as-quenched Fe-10at%B sample before and after laser processing.

sample and 47% for another. The grazing angle technique was used to determine the location of this crystalline material. As can be seen in Figure 26 the crystalline peaks were observed at angles as low as 2.5° which indicates there was crystalline material from the substrate to the top of the modified layer. A complete summary of the phases observed in the as-quenched samples before and after irradiation is presented in Table 2.

Each of the alloys in the range 10-30at%B was analyzed using the SSXD method. As shown in Figure 27, the volume fraction of crystalline material was quite small between 15 and 20at%B and increased with increasing departure from the eutectic composition. Figure 28 shows that the layer thickness of the melted region decreased with decreasing boron content away from the eutectic composition. The data plotted in Figure 27 were obtained by averaging several values of ν obtained from the set of implicit SSXD equations, when considering different pairs of diffraction lines for a given sample. The same ratios of pre-/post-irradiation intensities (R_i) together with the average ν were used to calculate a set of δ 's. The average of these values is the average thickness shown in Figure 28. The two values of δ at 10at%B and 15at%B correspond to two different samples that yield a very close value of ν .

Another group of as-quenched samples, all containing 20at%B, were irradiated at various energy densities ranging

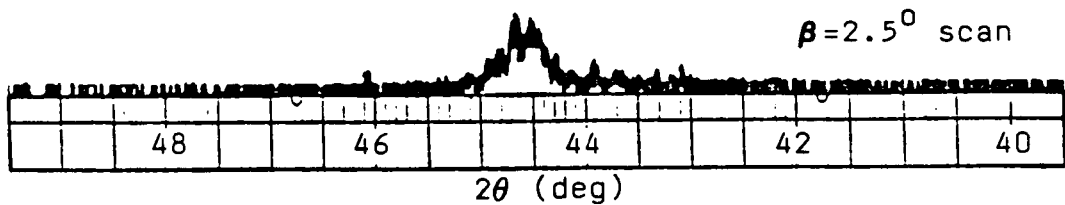
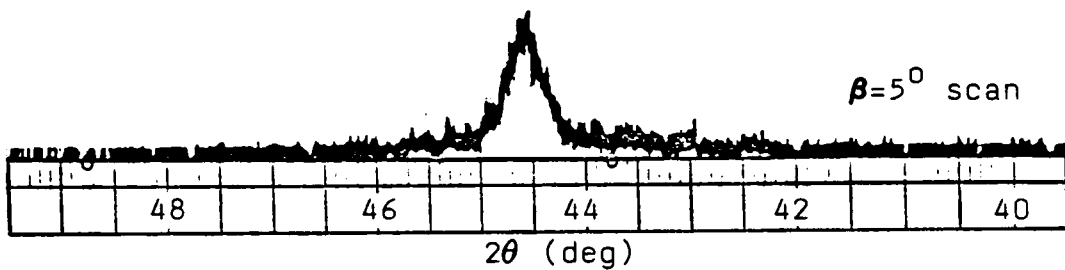
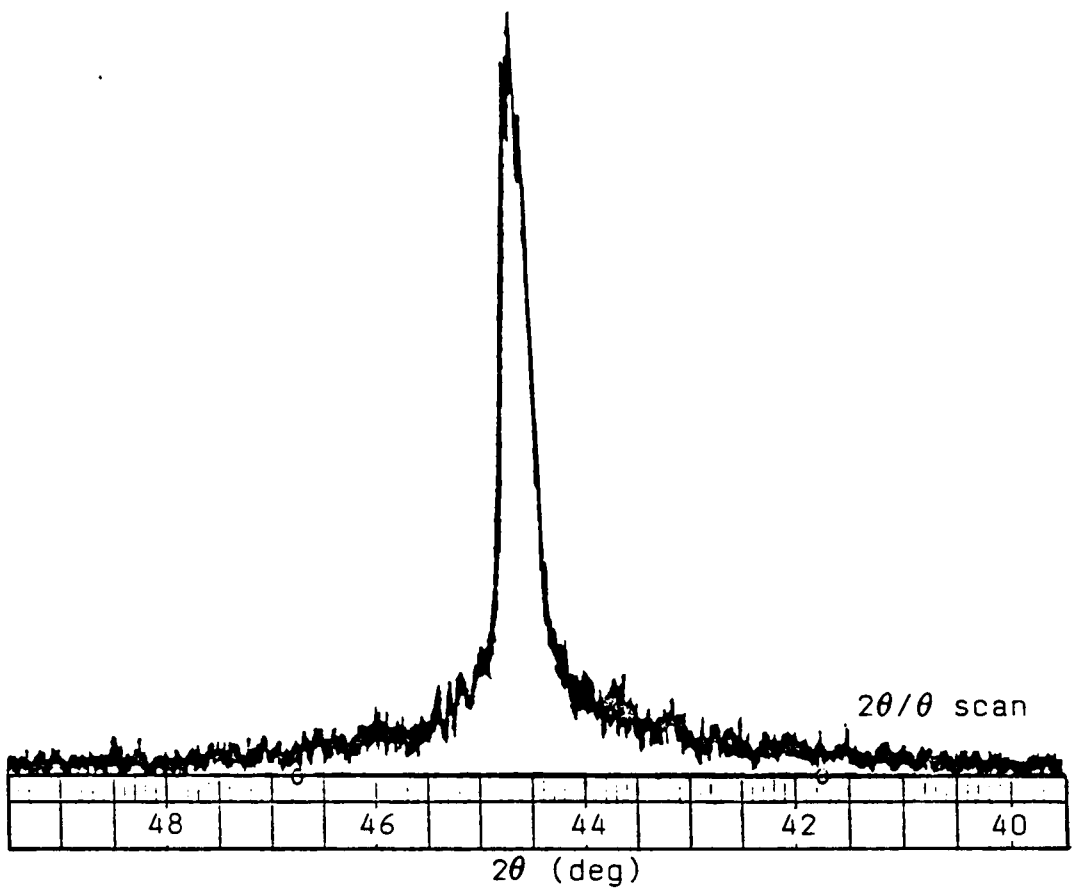


Figure 26. Grazing angle and parafofocussing geometry x-ray diffraction patterns for as-quenched, laser processed Fe-10at%B sample, showing the (110) α -iron peak.

TABLE 2 - Phases present in as-quenched iron-boron alloys prior to and following laser processing with 3 J/cm^2

Composition at. % Boron	Phases present prior to laser processing (120 mg sample)	Phases present after laser irradiation
5	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	$\alpha\text{-Fe} + \alpha'$
10	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	amorphous + $\alpha\text{-Fe} + \alpha'$
15	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$ $\text{Fe}_3\text{B (orthorhombic)}$	amorphous
20	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	amorphous
25	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$ $\text{Fe}_3\text{B (orthorhombic)}$	amorphous + $\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$
30	$\alpha\text{-Fe} + \text{Fe}_2\text{B (tetragonal)}$	amorphous + $\alpha\text{-Fe} + \text{Fe}_2\text{B}$

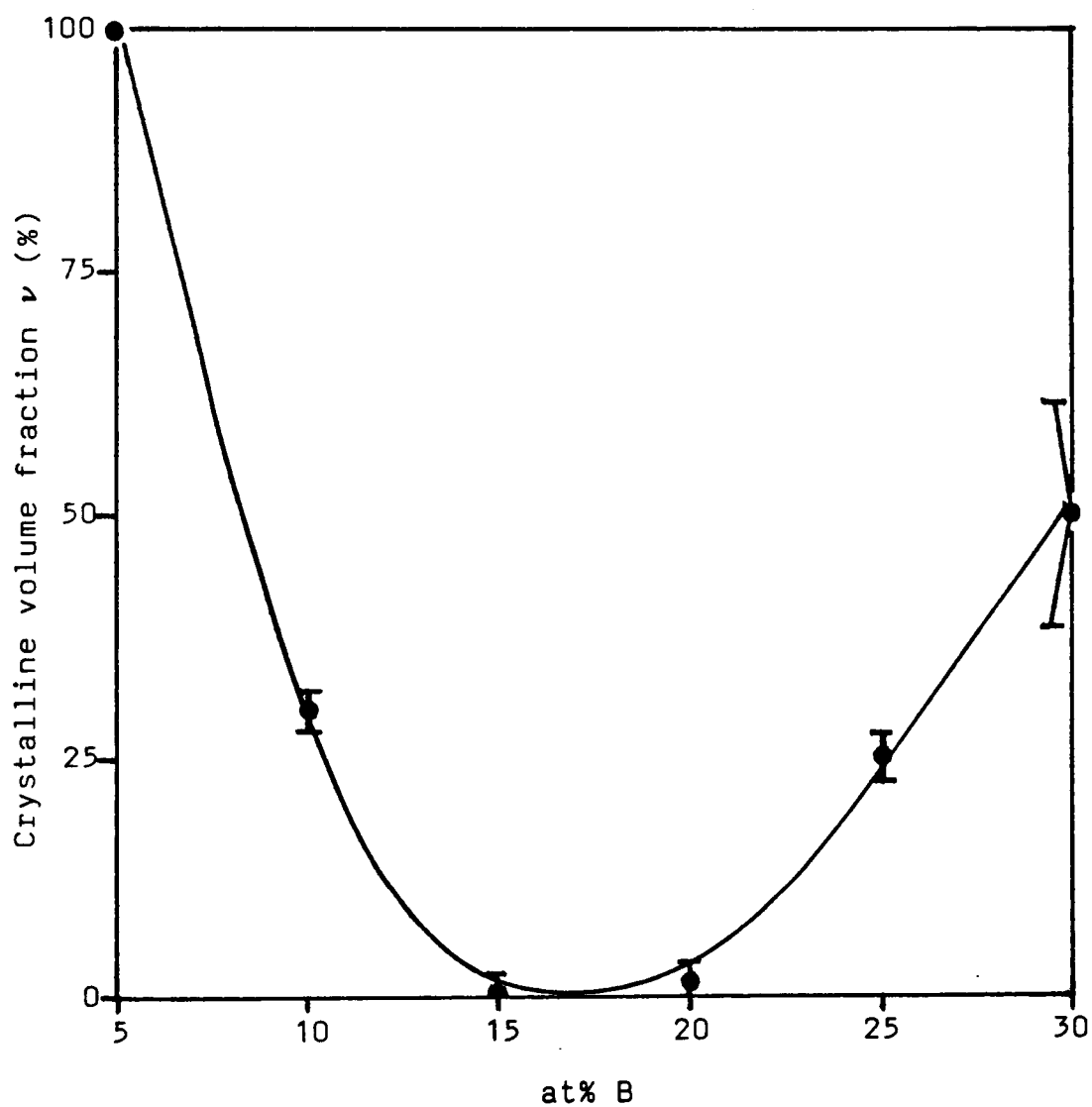


Figure 27. Volume fraction of crystalline material in the modified layer of laser processed as-quenched Fe-B alloys as a function of composition.

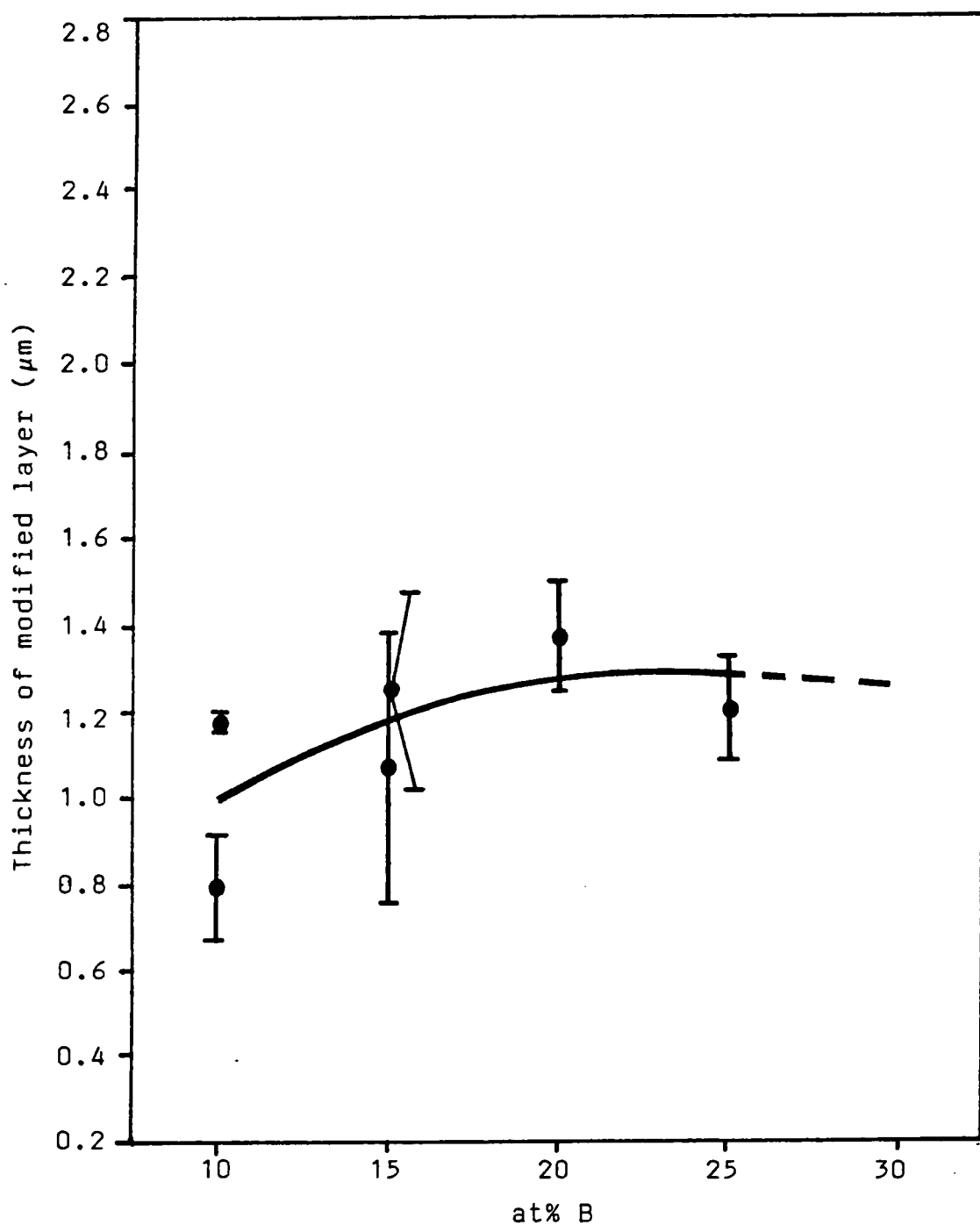


Figure 28. Thickness of the modified layer of laser processed Fe-B alloys as a function of composition.

from 0.5-3.5 J/cm². The average layer thickness was calculated for each energy density using the SSXD technique and is plotted in Figure 29. As can be seen, the melted layer thickness increases with increasing input energy up to about 3 J/cm². Above this energy the layer thickness increased at a much slower rate. Below about 1.25 J/cm², the measured thickness of the layer was zero. Analysis of these samples using the grazing angle technique showed that all the specimens which were irradiated with an energy density of 2.0 J/cm² or greater had no crystalline material present in the modified layer, whereas the sample irradiated with 1.5 J/cm² had both crystalline and amorphous present. No structural changes were observed for samples irradiated with 1.0 J/cm² or less.

Annealed Material

Characterization of Annealed Material

In all the samples, the most apparent change observed by x-ray analysis following the anneal was an increase in intensity and sharpening of the α -iron and boride lines. No phase transformation in the boride phases was observed to occur because of the anneal.

Laser Treatments of Annealed Material

The annealed samples were then irradiated using the XeCl laser with an energy density of 3J/cm². Analysis of

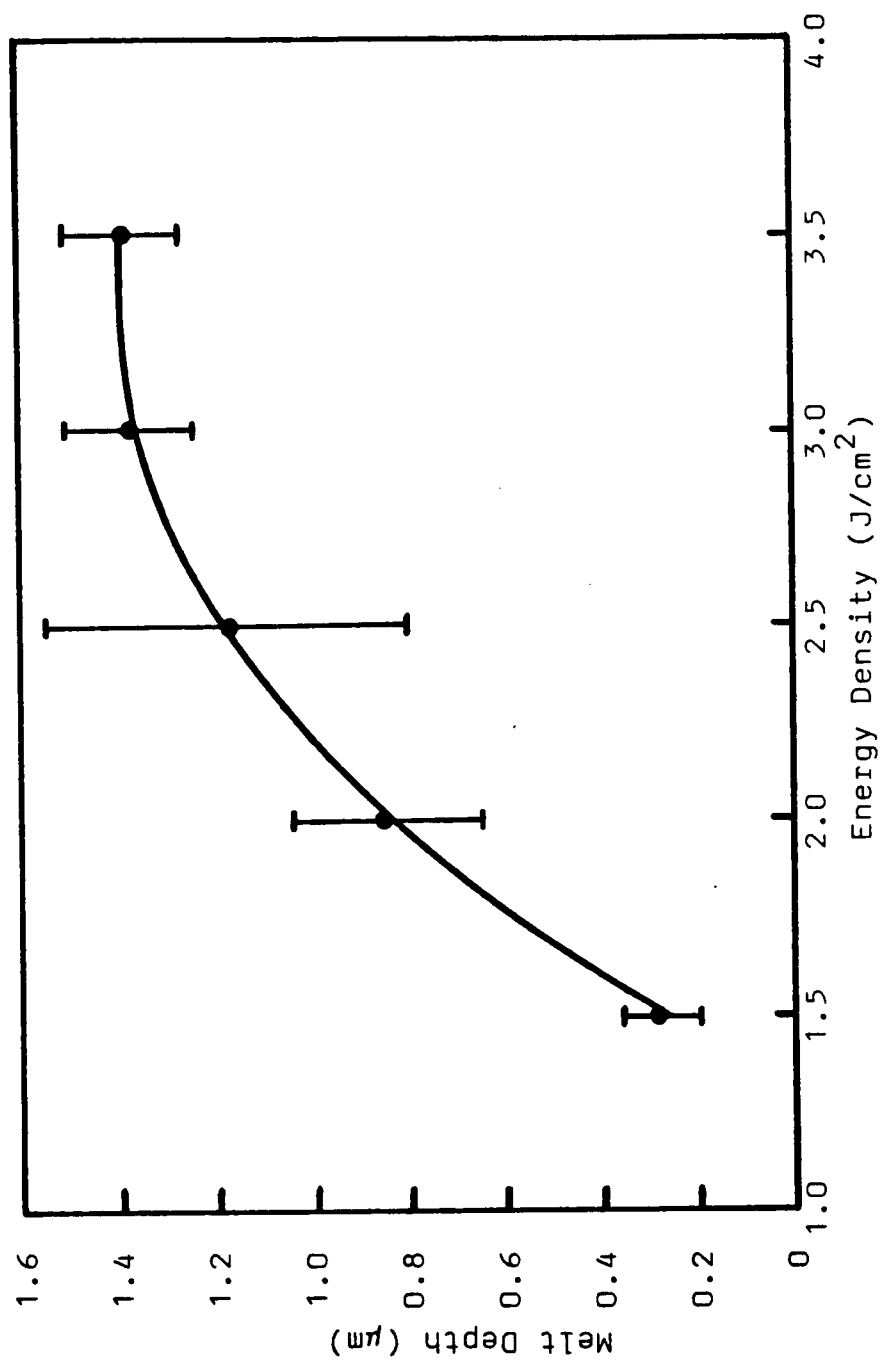


Figure 29. Melt depth of the modified layer as a function of the input energy density for as-quenched Fe-20at%B alloys.

the post-irradiation patterns indicated that very little, if any, amorphization occurred. The only change observed was a decrease in intensity and a broadening of the α -iron and boride lines. A complete summary of the observed phases in the annealed samples is presented in Table 3.

An attempt to amorphize an annealed 15at% sample with additional irradiations was only partially successful. The sample was irradiated with as many as four laser scans, but exhibited only a slight increase in the amount of amorphous material present in the modified layer.

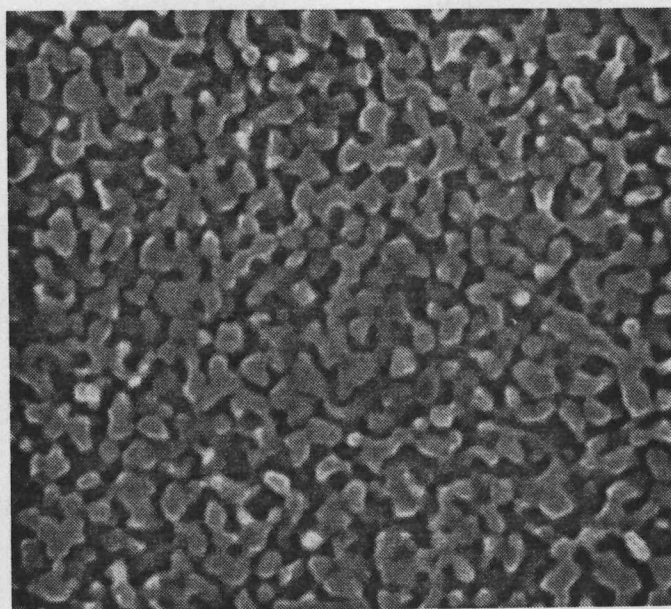
Microstructure Evaluation

Figures 30a and 31 show scanning electron micrographs of Fe-20at%B samples in the as-quenched and annealed conditions, respectively. Whereas in the as-quenched sample a fine dispersion of α -iron and borides with a particle size of about 0.05 μm can be seen, in the annealed sample the particle size is 0.5 μm . Since the same boride types were found in both samples, the different behavior upon laser annealing may be related to the difference in particle size.

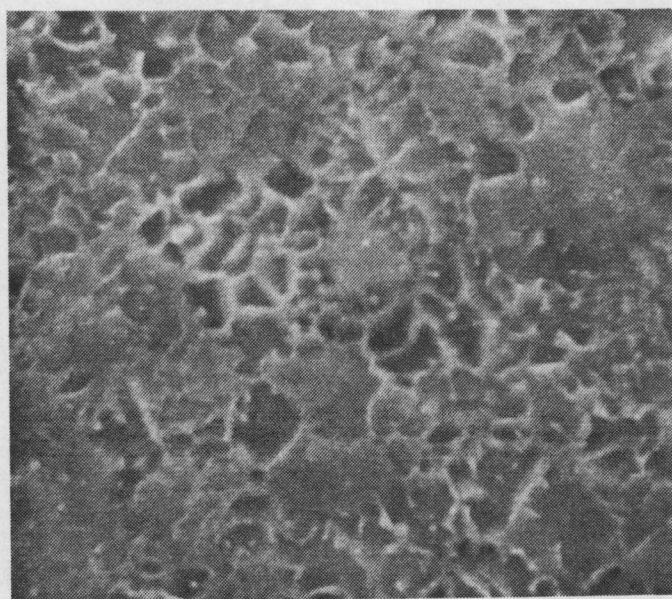
An increase in the size of the α -iron particles with decreasing boron content was seen in the as-quenched samples. Figure 30b shows the microstructure for the 5at% boron sample. The size of the α -iron particles was

TABLE 3 - Phases present in annealed iron-boron alloys prior to and following laser processing with 3 J/cm^2

Composition at. % Boron	Phases present prior to laser processing (120 mg sample)	Phases present after laser irradiation
5	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$
10	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$
15	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$
20	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$
25	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$	$\alpha\text{-Fe} + \text{Fe}_3\text{B (bct)}$
30	$\alpha\text{-Fe} + \text{Fe}_2\text{B (tetragonal)}$	$\alpha\text{-Fe} + \text{Fe}_2\text{B}$

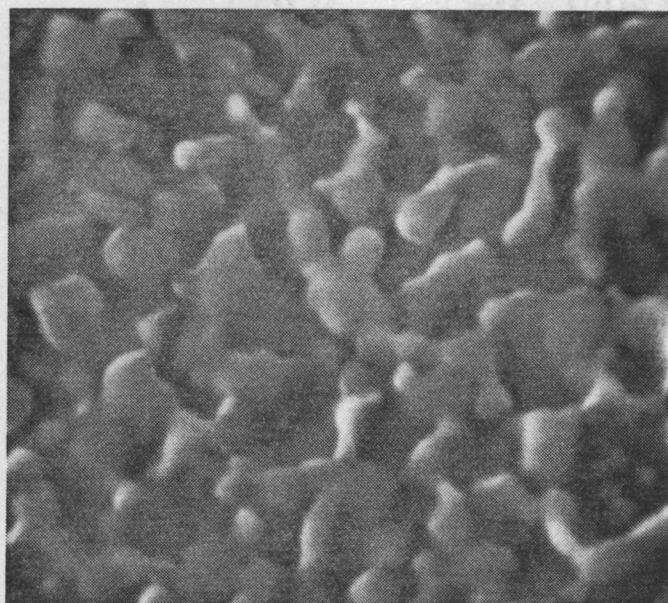


(a) | 0.5 μm |



(b) | 3 μm |

Figure 30. SEM micrograph of as-quenched iron-boron alloys
 (a) Fe-20at%B
 (b) Fe-5at%B



| 1 μm |

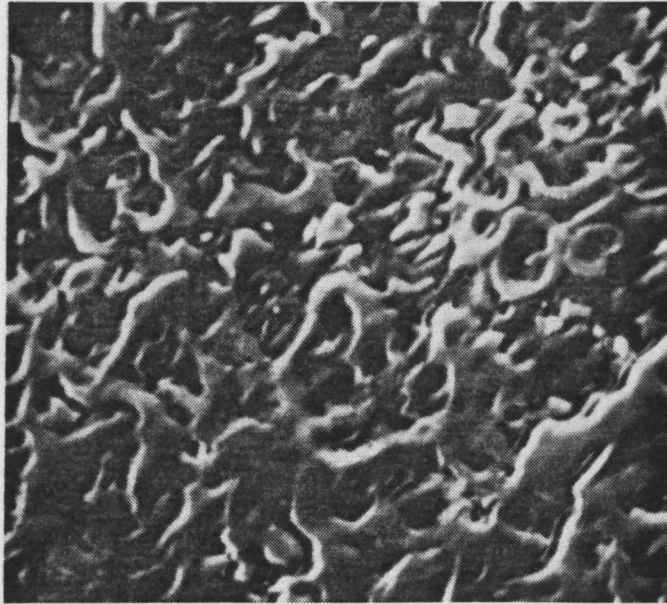
Figure 31. SEM micrograph of an Fe-20at%B sample in the annealed condition.

observed to be 1.0 μm , 0.50 μm and 0.05 μm for the 5at%, 10at% and 20at% boron samples respectively.

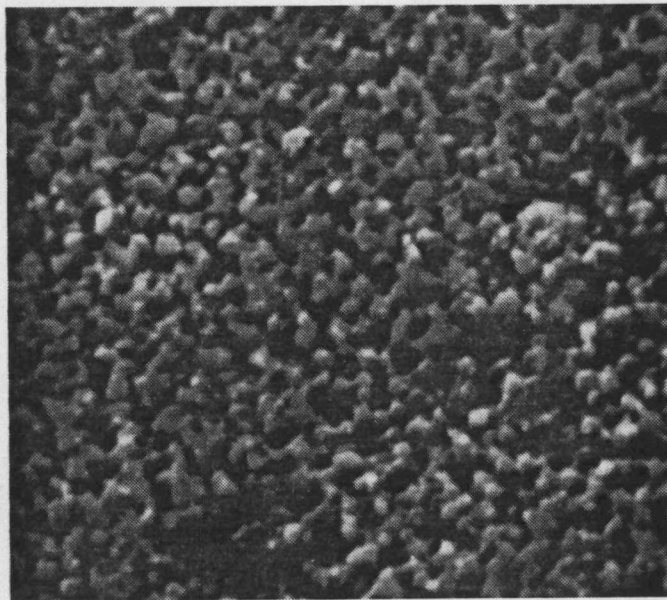
Figures 32a and 32b show the effect of additional laser processing on the microstructure of the annealed samples. Figure 32a shows the microstructure after one irradiation and Figure 32b shows the microstructure after four irradiations. The wormlike structure seen in Figure 32b indicated that epitaxial regrowth and nucleation of the α -iron prevented amorphization from occurring. The continued refinement of the microstructure with additional irradiations and the fact that amorphization was possible when the particle size was on the order of 0.05 μm indicated that mixing occurs in the molten layer during processing. Since the nanosecond laser melting is such an extremely fast process, diffusion in the solid state is certainly negligible. Further, as noted in earlier chapters, convective mixing in the liquid may also be neglected. Thus, while diffusional mixing in the liquid would be very limited due to the short times involved, it remains the only process by which these observations could be explained.

Diffusion Modeling

To evaluate this hypothesis, an analytical model was developed for calculating the diffusional mixing in the liquid. For the conditions of these experiments, the laser



(a) | 2 μm |



(b) | 2 μm |

Figure 32. SEM micrograph of an annealed Fe-20at%B alloy
(a) after one laser scan
(b) after four laser scans

melted region should be completely resolidified after about 100-200 ns. The model assumes that melting of both phases occurred readily and all mixing took place in the liquid. A cellular method was employed where cubic boride particles were embedded in α -iron for alloys of low boron concentration (5-10%), while for higher concentrations (20-25%), α -iron grains were embedded in borides. Using a Fourier analysis (see Appendix C), it was found that for the cases where the borides were embedded in the α -iron, the boron concentration C at a position x, y, z and time t is given by (McCmay, Pedraza and Lowndes, 1987)

$$C(x, y, z, t) = C_A + (C_B - C_A) C_1(x, y, z, t) \quad (26)$$

where $C_1(X, Y, Z, t)$ is given by

$$\begin{aligned} C_1(X, Y, Z, t) &= X(x, t) Y(y, t) Z(z, t) \\ &= \left\{ \frac{a}{b} + \frac{2}{n} \sum_1 \frac{1}{\ell} \sin\left(\frac{\ell n a}{b}\right) \cos\left(\frac{\ell n x}{b}\right) e^{-\frac{\ell^2 n^2}{b^2} D t} \right\} \\ &\cdot \left\{ \frac{a}{b} + \frac{2}{n} \sum_1 \frac{1}{m} \sin\left(\frac{m n a}{b}\right) \cos\left(\frac{m n y}{b}\right) e^{-\frac{m^2 n^2}{b^2} D t} \right\} \\ &\cdot \left\{ \frac{a}{b} + \frac{2}{n} \sum_1 \frac{1}{n} \sin\left(\frac{n n a}{b}\right) \cos\left(\frac{n n z}{b}\right) e^{-\frac{n^2 n^2}{b^2} D t} \right\} \end{aligned} \quad (27)$$

C_A and C_B are respectively the boron concentrations in the ferrite and the boride phases, a and b are the sizes of the cubic particles and the embedding medium and D is the diffusion coefficient of boron in the liquid. A computer program, written in Fortran, was used to calculate the boron distribution for different particle sizes. Another program, written in Basic (Appendix D) for use on a PC was used to determine the composition at the crystal/amorphous interface.

For the Fe-20at%B alloy, if the particle size is $0.5 \mu\text{m}$ (e.g. annealed sample) no appreciable mixing occurs in the liquid, i.e., regions which were borides or ferrite before melting, remained essentially the same after 100ns. On the other hand, the calculations indicated that for a specimen with the same composition, but having a $0.05 \mu\text{m}$ particle size, the melt would be completely homogeneous after 100ns.

Furthermore, the crystalline volume fraction, ν , can be expressed as

$$\nu = 1 - \Omega/b^3 \quad (28)$$

where Ω is the amorphous volume within the embedding cell. The experimentally determined value of Ω was used in the diffusion equations above to determine what the lowest boron concentration is which prevents nucleation and epitaxial regrowth. Using the experimental value of $\nu=0.3$

from the 10at%B specimen, it was determined that epitaxial regrowth and nucleation occurred in the regions with less than 5.3at%B.

CHAPTER VI

SUMMARY AND DISCUSSION

SSXD Technique

The primary purpose of this work was to study the amorphization of iron-boron alloys by laser processing. A new surface sensitive x-ray diffraction technique (SSXD) was developed to analyze the modified layer which was produced. This method is quite general in nature, and may be used to analyze any processed layer whose diffraction peaks are different from those of the underlying substrate. With this technique we were able to determine the thickness of the modified layer and the volume fraction of crystalline material within that region and thus quantify the extent to which amorphization had occurred. The accuracy of this technique was evaluated by independent measurement of the amorphous layer thickness on an Fe-20at%B specimen using SEM.

As-Quenched Material

During sample preparation, it was found that all the samples which weighed more than about 0.08 g formed a mixture of metastable Fe_3B and α -iron when splat quenched. However, when a sample of Fe-20at%B weighing 0.04 g was quenched, a mixture of Fe_3B , α -iron and amorphous Fe-B was

formed. In addition, it was found that the thickness of the 0.04 g sample was about 10 μm , while samples weighing about 0.10 g had a thickness of about 40 μm . Since the experimental procedure was the same for all runs, it would appear that the increase in cooling rate required to form the amorphous phase occurred due to the decrease in sample weight and a corresponding reduction in sample thickness. This is in agreement with Miyazawa and Szekely (1979), who showed that the cooling rate increased as the thickness of the splat decreased. They reasoned that by lowering the weight, the resulting quenched sample would be thinner and the cooling rate higher.

Examination of the microstructure of the as-quenched samples showed that the grain size of the α -iron particles increased as the boron content decreased. This compositional dependence can be evaluated by examining the crystal growth as a thermally driven process.

The growth velocity of a crystalline phase can be written as (Christian, 1965)

$$U = f d v \frac{\Delta G}{T} e^{\frac{-Q}{RT}} \quad (29)$$

the precipitate size, then, is

$$L = f d v t \frac{\Delta G}{T} e^{\frac{-Q}{RT}} \quad (30)$$

The range of temperatures at which this growth can occur is bounded above by the equilibrium liquidus line and

below by the T_0 line. The T_0 line is the locus of points where the free energy of the liquid is equal to the free energy of the solid and, at temperatures less than T_0 , the solidification will be partitionless.

Since the cooling rate for splat quenching is on the order of 10^6 K/s the temperatures at which crystal growth occurs during splat quenching should lie well below the equilibrium liquidus line. Further, because only a small decrease in sample weight was required before the amorphous structure was produced, it would seem that the crystal growth process occurs at temperatures only slightly greater than the glass transition temperature (T_g), thus it is assumed that the growth occurs at temperatures along a line drawn between the melting point of pure iron and the T_g temperature for the Fe-20at%B alloy. The estimated T_g for Fe-20at%B is 723 K (Cowlam and Carr, 1985), the temperatures, then, for the compositions of interest, 5at%B, 10at%B and 20at%B are respectively, 1537 K, 1265 K and 723 K, all of which lie between the equilibrium liquidus and above the T_0 line (Figure 33) as required. A least squares fit of the logarithm of the precipitate size versus $1/T$ yields a straight line (coefficient of correlation, $r^2=0.998$). The slope of this line yields a value for the activation energy of 33,500 J/mole.

Using this fit, values for the precipitate size were calculated and compared with the actual data (Table 4). As

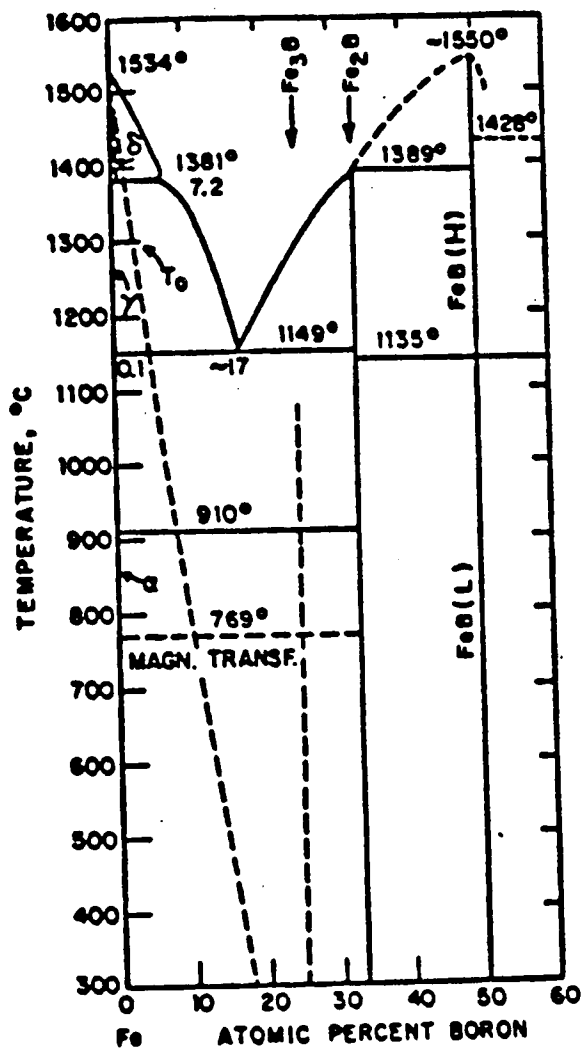


Figure 33. Fe-B phase diagram with the T_0 line calculated using a regular solution approximation. (Lin, 1983)

can be seen, the agreement is quite good, indicating that the thermally driven crystal growth approach can describe the compositional dependency of the variation in the precipitate size of the as-quenched samples.

TABLE 4 - Precipitate size of as-quenched iron-boron alloys as a function of boron content; experimental data and values calculated based on the thermally driven crystal growth approach.

Composition at. % Boron	Actual Precipitate Size (um)	Calculated Precipitate Size (um)
5	1.00	0.94
10	0.50	0.54
20	0.05	0.05

When laser processed, as-quenched specimens with 15 and 20at%B became completely amorphous, while partial amorphization occurred in the samples containing 10, 25 and 30at%B. No amorphization occurred in any of the samples containing 5at%B.

X-ray analysis of the 5at%B samples revealed a second set of peaks which were produced by a bcc structure having a lattice parameter of 0.2840 nm. Ray and Hasegawa (1978) measured a lattice parameter of 0.2863 nm for a metastable

Fe-6at%B alloy. From measurements of the saturation moment and Curie temperature they concluded that two iron atoms were replaced by three boron atoms. The lower lattice parameter obtained in our work implies that all the boron atoms are substitutional in solid solution. The lattice parameter for a Fe-5at%B solid solution was calculated using Vigard's law and assuming each boron atom substitutes for one iron atom. The Fe-B interatomic distance used in the calculation was that obtained from the RDF data for an Fe-20at%B amorphous sample by Nold, et al. It was assumed that the Fe-B bond length would be the same in both the glass and the solid solution. This calculation showed that a Fe-5at%B solid solution will have a lattice parameter of 0.2847 nm which agrees well with that for the α' phase.

This phase is most probably the same one observed by Lin (1983) when a 5at%B sample was irradiated with a picosecond laser. Lin indexed the crystals he observed as bcc, but was unable to determine the lattice parameter. However, he reasoned that since the lattice parameter for the bcc Fe-5at%B structure is so close to that of α -iron, Fe-5at%B crystals could grow epitaxially from a pre-existing α -iron crystal. This hypothesis is consistent with our results since the α -iron in the substrate of our samples contains about 2.5at%B in solution and thus has a lattice parameter only 0.9% larger than that of a Fe-5at%B bcc structure. Further, analysis of the 5at%B sample using the grazing

angle technique indicated that the modified layer was composed predominantly of this second phase, with little or no α -iron.

The experimental lower compositional limit for which amorphization of as-quenched and laser processed iron alloys was found to lie between 5-10at%B. An upper limit of about 40at%B is found by extrapolation of the data in Figure 27, page 79. Using an analytical model to describe the homogenization of the melt, it was found that for boron concentrations less than 5.3at%, epitaxial regrowth and nucleation would occur rather than amorphization, which is consistent with the result from the 5at%B samples. Below this limit the velocity of the crystalline growth interface exceeds the velocity of a solidification interface controlled by heat removal. For a melt depth of 1.2 μm and a solidification time of 70 ns, the solidification velocity is approximately 17 m/s. Spaepen (1986) has computed the crystal growth speed as a function of boron content. As shown in Figure 4, page 17, a velocity of 17 m/s corresponds to a composition of 4.8at%B, which is quite close to the value determined by our model. The ferrite grain size of the splat quenched specimens increases with decreasing boron content and limits the degree of homogenization that occurs in the melt. This then imposes a practical limit on the extent to which amorphization can occur in low boron splat quenched specimens.

Annealed Material

Analysis of the annealed samples indicated that little or no amorphization occurred when they were irradiated. Comparison of the annealed and as-quenched microstructures using SEM revealed that the α -iron and boride particles in the annealed samples were an order of magnitude larger than those in the as-quenched samples. The same boride types were detected by x-ray diffraction analysis in both groups of samples, implying that the short annealing produced mainly particle coarsening. The different behavior upon laser treatment is thus related to the difference in particle size. To evaluate this hypothesis an analytical model, described in Appendix C, was used to study the mixing in the liquid. The model assumes that melting of both phases occurs readily, all mixing takes place in the liquid and that the melting and resolidification process lasts 70-150 ns. It was found that for the annealed 20at%B alloy, which had a particle size of 0.5 μm , no appreciable mixing in the liquid occurs, i.e., regions that were borides or ferrite before melting, remain essentially the same after 100 ns. In this case then, epitaxial regrowth and nucleation of α -iron in the low-boron regions of the liquid occurs, preventing amorphization. The lower melting borides then solidify in the spaces between the α -iron grains. If the spacing is

large enough, the borides would be interconnected, forming a tortuous network between the α -iron grains. A second irradiation would serve to allow further diffusion to occur, reducing the spacing between the α -iron grains. If sufficient diffusion occurs, the spacing would be reduced so that the borides would no longer be connected and the borides would solidify as individual grains. Additional irradiations would further reduce the spacing between the α -iron grains, resulting in smaller boride grains. This was confirmed by the presence of interconnected, vermiform boride particles in the microstructure of a specimen which had been irradiated once. In regions which had been irradiated more than once, single, equiaxed borides were observed. Further refinement of these grains occurred as the number of irradiations was increased.

On the other hand, model calculations indicated that for the as-quenched 20at%B sample, which had a particle size of 0.05 μm , the melt is completely homogeneous after 100 ns. This melt has a much lower solidification point than the inhomogeneous one of the previous case, and, as discussed earlier, the higher boron content of the liquid slows the interface mobility making amorphization possible.

As-quenched 20at%B samples were laser processed with energy densities ranging from 0.5-3.5 J/cm^2 and then analyzed with the SSXD method to determine the thickness of the melted layer. As expected, lower melt depths were

associated with lower energy densities while the depth of melting tends to saturate at higher fluences. The process efficiency may be defined as the depth melted per unit power input and is shown in Figure 34. As can be seen, the optimal process efficiency lies between 2.5 J/cm^2 and 3.0 J/cm^2 . Below this optimal point a greater proportion of the incident energy is removed by conduction, while above it, the additional energy added is not conducted away nor used to extend the melt zone. When this occurs, the temperature at the surface exceeds the melting point and evaporation and plasma formation occurs. This phenomenon has been observed for pure iron (Godbole) and copper (Walter, et al.)

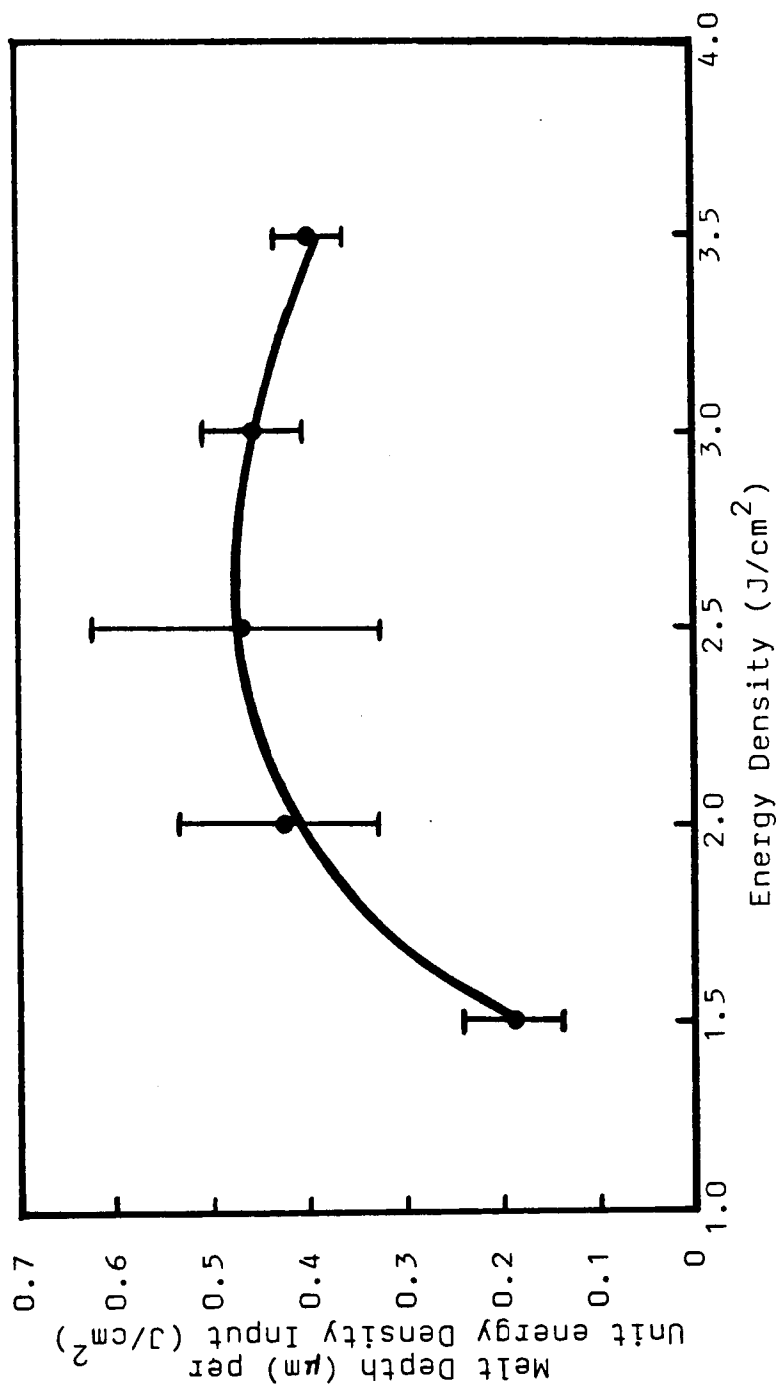


Figure 34. Process efficiency, measured as melt depth per unit energy density input, as a function of energy density for an as-quenched Fe-20at%B sample.

CHAPTER VII

CONCLUSIONS

- 1) Processing of as-quenched Fe-5at%B alloys using a nanosecond excimer laser produces a bcc phase with a lattice parameter 0.9% less than that of pure iron.
- 2) The initial microstructure plays a fundamental role during pulsed laser processing inasmuch as compositional inhomogeneities that may remain in the liquid determine the resulting structure. The ferrite grain size in splat quenched iron alloy specimens increase with decreasing boron content, imposing a practical limit on the extent to which amorphization can occur in low boron alloys.
- 3) The microstructure of annealed Fe-B alloys is refined with repeated laser processing.
- 4) The surface sensitive x-ray diffraction technique can be used to determine the melt depth and crystalline volume fraction of laser processed Fe-B alloys.
- 5) Amorphization was observed in as-quenched Fe-B alloys with 10-30at%B are processed with a nanosecond excimer laser. However, only those samples with 15-20at%B show complete amorphization, all other compositions show only partial amorphization.

6) The experimental evidence, together with the developed analytical model, gives 5.3at%B as the lower limit for amorphization by nanosecond laser processing. Extrapolation of experimental data yields an upper limit of 40at%B.

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APPENDICES

APPENDIX A

Table A.1 - Distance between lattice planes (d-space) and resulting Bragg angle reflections for Fe_2B , bct phase, CuAl_2 type, $a=5.11$ nm, $b=4.25$ nm, using a Cu x-ray target

Lattice plane (hkl)	d-space (nm)	K_α Bragg reflection (2θ degrees)
110	0.3613	24.637
101	0.3268	27.269
200	0.2555	35.122
002	0.2125	42.504
211	0.2013	45.040
112	0.1832	49.778
220	0.1807	50.156
202	0.1634	56.308
310	0.1616	56.987
301	0.1581	58.363
222	0.1376	68.121
103	0.1365	68.761
321	0.1344	69.972
312	0.1286	73.643
400	0.1278	74.233
330	0.12044	79.590
213	0.12041	79.619
411	0.1190	80.770

Table A.2 - Distance between lattice planes (d-space)
and resulting Bragg angle reflections for
 Fe_3B , bct phase. Ti_3P type, $a=8.64$ nm,
 $b=4.28$ nm, using a Cu x-ray target

Lattice plane (hkl)	d-space (nm)	K_α Bragg reflection (2θ degrees)
110	0.6102	14.515
200	0.4320	20.559
101	0.3835	23.191
220	0.3055	29.235
211	0.2868	31.158
310	0.2732	32.777
301	0.2389	37.644
400	0.2160	41.819
002	0.2140	42.229
321	0.2091	43.270
330	0.2036	44.487
112	0.2020	44.877
420	0.1932	47.034
202	0.1918	47.407
411	0.1882	48.360
222	0.1753	52.186
510	0.1694	54.124
312	0.1685	54.561
501	0.1602	57.515
440	0.1527	60.626
402	0.1520	60.940
521	0.1502	61.746
530	0.1482	62.699
332	0.1475	63.007
600	0.1440	64.734
422	0.1434	65.037
103	0.1408	66.414
620	0.1366	68.707
611	0.1348	69.756
213	0.1338	70.340
512	0.1328	70.943
541	0.1287	73.601
303	0.1278	74.172

Table A.3 - Distance between lattice planes (d-space) and resulting Bragg angle reflections for Fe_3B , orthorhombic phase. Fe_3C type, $a=5.11$ nm, $b=4.25$ nm, $c=4.45$ nm, using a Cu x-ray target

Lattice plane (hkl)	d-space (nm)	K_α Bragg reflection (2θ degrees)
100	0.5430	16.324
001	0.4450	19.952
110	0.4208	21.110
011	0.3700	24.051
101	0.3442	25.885
020	0.3330	26.771
111	0.3058	29.206
120	0.2839	31.515
200	0.2715	32.991
021	0.2666	33.613
210	0.2514	35.712
121	0.2393	37.582
201	0.2318	38.855
002	0.2225	40.543
030	0.2220	40.638
211	0.2189	41.241
012	0.2110	42.851
220	0.2104	42.981
102	0.2059	43.978
130	0.2055	44.067
031	0.1987	45.668
112	0.1967	46.147
221	0.1902	47.813
131	0.1866	48.814
022	0.1850	49.252
300	0.1810	50.416
122	0.1751	52.235
310	0.1747	52.381
202	0.1721	53.225
230	0.1719	53.302
301	0.1677	54.747
212	0.1666	55.118
040	0.1665	55.162
311	0.1626	56.606
231	0.1603	57.481
140	0.1592	57.930
320	0.1590	57.993

Table A.4 - Distance between lattice planes (d-space)
and resulting Bragg angle reflections for
 Fe_{23}B_6 , fcc phase. $a=10.67$ nm,
using a Cu x-ray target

Lattice plane (hkl)	d-space (nm)	K_α Bragg reflection (2θ degrees)
111	0.6160	14.377
200	0.5335	16.616
220	0.3772	23.583
311	0.3217	27.728
222	0.3080	28.988
400	0.2667	33.596
331	0.2448	36.713
420	0.2386	37.702
422	0.2178	41.458
511	0.2053	44.100
440	0.1886	48.246
531	0.1804	50.609
600	0.1778	51.379
620	0.1687	54.380
533	0.1627	56.558
622	0.1609	57.272
444	0.1540	60.073
711	0.1494	62.123

APPENDIX B

The parafofocussing geometry is shown schematically in Figure 16. For this specimen arrangement the intensity of each diffracted beam is given by (Cullity, 1978)

$$dI_D = \frac{I_0 ab}{\sin\theta} \exp\left(-\frac{2\mu x}{\sin\theta}\right) dx \quad (B.1)$$

where I_0 is the intensity of the incident beam, a is the specimen volume fraction with the correct orientation for diffraction, b is the fraction of I_0 that is diffracted per unit volume, μ is the linear absorption coefficient, θ is the Bragg angle and x is the penetration distance normal to the specimen surface.

The linear absorption coefficient of an Fe-B substrate, μ , and of the upper modified layer, μ' , are (Cullity)

$$\mu = \left\{ \left(\frac{\mu}{\rho}\right)_{Fe} w_{Fe} + \left(\frac{\mu}{\rho}\right)_B w_B \right\} \rho \quad (B.2)$$

and

$$\mu' = \left(\frac{\mu}{\rho}\right) \rho' \quad (B.3)$$

where w_{Fe} and w_B are respectively the weight fractions of iron and boron in the material and $(\mu/\rho)_A$ is the mass absorption coefficient of element A. The densities ρ and ρ' are found by

$$\frac{1}{\rho} = \frac{1}{\rho_a} w_a + \frac{1}{\rho_\beta} w_\beta \quad (\text{B.4})$$

where ρ_α , ρ_β are the densities of the α and β phases, while w_α , w_β are the corresponding weight fractions in the substrate and ρ_c is the density of the crystalline portion and ρ_a that of the amorphous one.

The mass absorption coefficients for iron and boron are $304.4 \text{ cm}^2/\text{g}$ and $2.142 \text{ cm}^2/\text{g}$ respectively (Cullity.) The density of amorphous Fe-20at%B was found by Ray, et al (1977) to be 7.5 g/cm^3 . Thus, when the crystalline volume fraction present in the modified layer (ν') is zero

$$\mu' = 2178.4 \text{ cm}^{-1}$$

For the contribution from the surface layer (denoted by ' l' ') of thickness δ , integration of the diffraction equation above yields

$$I_d = \frac{I_o b}{2\mu'} \nu a_i^t \left\{ 1 - e^{-2\mu'\delta/\sin \Theta} \right\} \quad (\text{B.5})$$

The contribution from the substrate (denoted by ' s' ') is next obtained by first considering that the incident beam on it has an intensity equal to

$$I_o' = I_o e^{-\mu'\delta/\sin \Theta} \quad (\text{B.6})$$

Therefore, the intensity of the beam diffracted from the substrate that reaches the interface with the upper (modified) layer is

$$I_d' = \frac{I_o' b}{2\mu} a_i^s \quad (\text{B.7})$$

However, this intensity is further attenuated by a factor of $\exp(-\mu\delta/\sin\theta)$ when the beam passes back through the upper layer. Therefore, the total diffracted intensity from a sample with a modified surface layer is

$$I_d' = \frac{I_o' b}{2\mu} \left\{ \frac{\mu}{\mu'} a_i^\ell v \left[1 - \exp\left(-\frac{2\mu'\delta}{\sin\Theta}\right) \right] + a_i^s \exp\left(-\frac{2\mu'\delta}{\sin\Theta}\right) \right\} \quad (\text{B.8})$$

For a thick and uniform sample (i.e. unmodified) the diffracted intensity is

$$I_d = \frac{I_o' ab}{2\mu} \quad (\text{B.9})$$

The ratio of intensities before and after the layer has been formed is

$$R_i = \frac{I_d'}{I_d} = r_i^\ell v' [1 - \exp(-\frac{2\mu'\delta}{\sin\Theta})] + r_i^s \exp(-\frac{2\mu'\delta}{\sin\Theta}) \quad (\text{B.10})$$

where

$$r_i^{\ell,s} = \frac{a_i^{\ell,s}}{a_i} \quad \text{and} \quad v'\mu' = v\mu \quad (\text{B.11})$$

gives the change in preferred orientation in the specimen after the layer was produced. The conditions under which this system of equations is solvable can now be analyzed.

The case where the orientation of the crystals embedded in the amorphous layer is the same as that of the substrate and no changes have occurred relative to the crystalline orientation in the substrate will be considered first. This assumption applies whether the crystalline orientations are or are not randomly distributed. The system of equations above can then be solved to give an implicit equation for ν

$$R_2 - \nu' = (R_1 - \nu')^{n_{12}} (1 - \nu')^{1 - n_{12}} \quad (\text{B.12})$$

where

$$n_{12} = \frac{\sin \Theta_1}{\sin \Theta_2} \quad (\text{B.13})$$

and the indexes 1,2 refer to any two peaks. It is seen that $\nu=1$ only when the value of both ratios are unity, while $\nu=0$ when $R_2 = R_1^{n_{12}}$.

The thickness, δ , can then be obtained from

$$\delta = \frac{\sin \Theta_i}{2\mu'} \ln \left(\frac{1 - \nu'}{R_i - \nu'} \right) \quad (\text{B.14})$$

using any ratio and the corresponding Bragg angle.

In the situation where the layer is fully amorphous (i.e. $\nu=0$)

$$R_i = r_i^s \exp\left(-\frac{2\mu'\delta}{\sin\Theta_i}\right) \quad (\text{B.15})$$

then, selecting two diffraction peaks that will have the same value of r_s (e.g. (110) and (220) in a bcc material), the value of δ can be determined from

$$\delta = \frac{P}{2\mu'} \ln \frac{R_1}{R_2} \quad (\text{B.16})$$

where

$$P = (\sin\Theta_2)^{-1} - (\sin\Theta_1)^{-1} \quad (\text{B.17})$$

If the crystalline orientation of the substrate has not changed, on the average, then $r_i=1$ for all the peaks and

$$\delta = \frac{\sin\Theta_i}{2\mu'} \ln R_i^{-1} \quad (\text{B.18})$$

yields an independent evaluation from each line. The multiplicity of lines thus offers the possibility of testing the validity of the assumptions made and also of assessing the measurement error.

In the most general situation where all the r_i 's are different and $\nu=0$, the system of equations does not allow for a determination of δ .

An independent method of computing the thickness of an amorphous layer, which applies in every case, is to integrate the area under the diffuse halo obtained in the diffraction pattern of the specimen and compare it with the integrated intensity of the halo of a fully amorphous sample of the same composition. The ratio of the two intensities is

$$R_a = \frac{I_a^\delta}{I_a} = \frac{\int_{\theta_a - \Delta\theta}^{\theta_a + \Delta\theta} b'(\theta) \left[1 - \exp \left\{ -\frac{2\mu'\delta}{\sin \theta} \right\} \right] d\theta}{\int_{\theta_a - \Delta\theta}^{\theta_a + \Delta\theta} b'(\theta) d\theta} \quad (\text{B.19})$$

where θ_a is the angle around which the halo is centered, 2θ is the angular extension of the halo and b' is the fraction of energy diffracted per unit angle θ . In the case of the Fe-20at%B alloy, which was considered with this technique, it was noted that $b'(\theta)$ is an approximately symmetric function of θ about θ_a . When the exponential factor above varies linearly with θ in the integration interval $2\Delta\theta \approx 6^\circ$, the following approximation may be used

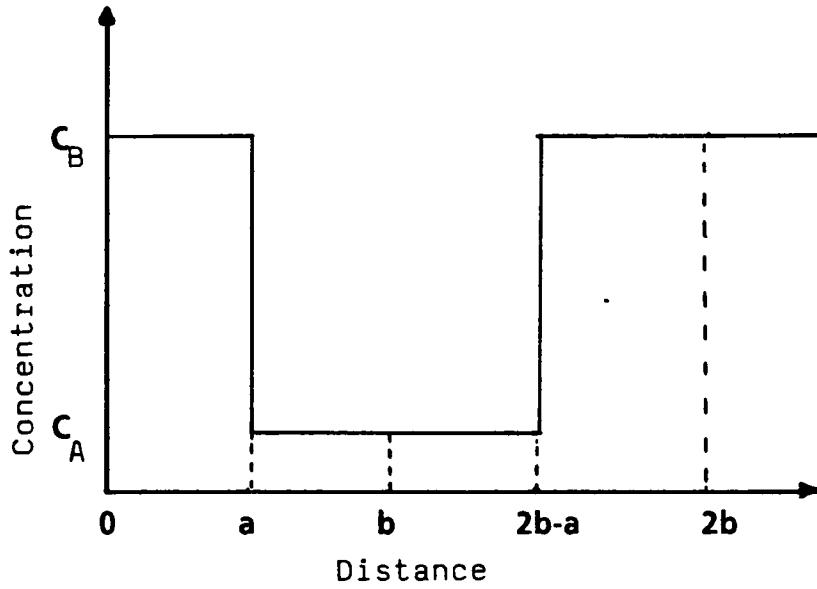
$$\int_{\theta_a - \Delta\theta}^{\theta_a + \Delta\theta} b'(\theta) \exp \left\{ -\frac{2\mu'\delta}{\sin \theta} \right\} d\theta \approx \exp \left\{ -\frac{2\mu'\delta}{\sin \theta_a} \right\} \int_{\theta_a - \Delta\theta}^{\theta_a + \Delta\theta} b'(\theta) d\theta \quad (\text{B.20})$$

In this approximation

$$\delta = \frac{\sin \Theta_a}{2\mu'} \ln (1 - R_a)^{-1} \quad (\text{B.21})$$

When the amorphous fraction is very small, the error in calculating the magnitude of R_a (or I_u) with this last method is large because it is obtained by deconvoluting the curve under a crystalline peak. Therefore, in this case, the calculation of δ by solving the system of equations above is clearly more accurate.

Appendix C



The initial structure shown above is cellular with embedded particles at the origin and at intervals of $(2\ell b, 2mb, 2nb)$ where ℓ, m and n are integers.

The diffusion equation is given by

$$D \nabla^2 C = \frac{\partial C}{\partial t} \quad (C.1)$$

Letting

$$C = T(t) + \phi(x, y, z) \quad (C.2)$$

By separation of variables we get

$$T'(t) + D\lambda^2 T(t) = 0 \quad (C.3)$$

For which

$$T(t) = e^{-\lambda^2 D t} \quad (C.4)$$

and

$$\nabla^2 \phi + \lambda^2 \phi = 0 \quad (C.5)$$

Letting

$$\phi = X(x) Y(y) Z(z) \quad (C.6)$$

We obtain

$$\frac{1}{X(x)} \frac{\partial^2 X}{\partial x^2} + \frac{1}{Y(y)} \frac{\partial^2 Y}{\partial y^2} + \frac{1}{Z(z)} \frac{\partial^2 Z}{\partial z^2} = -\lambda^2 \quad (C.7)$$

Since the function C is even, the solutions are

$$X(x) = \sum X_\ell \cos \alpha_\ell x + \frac{X_0}{2} \quad (C.8a)$$

$$Y(y) = \sum Y_m \cos \beta_m y + \frac{Y_0}{2} \quad (C.8b)$$

$$Z(z) = \sum Z_n \cos \gamma_n z + \frac{Z_0}{2} \quad (C.8c)$$

For which

$$X_0 = \frac{2}{b} \int_0^b f(x, 0) dx = \frac{2a}{b} \quad (C.9a)$$

similarly

$$Y_0 = \frac{2a}{b} \text{ and } Z_0 = \frac{2a}{b} \quad (C.9b), (C.9c)$$

The solutions for X_ℓ , Y_m and Z_n are found from

$$X_\ell = \frac{2}{b} \int_0^b f(x, 0) \cos \left(\frac{\ell \pi x}{b} \right) dx = \frac{2}{\ell \pi} \sin \left(\frac{\ell \pi a}{b} \right) \quad (C.10a)$$

$$Y_m = \frac{2}{m \pi} \sin \left(\frac{m \pi a}{b} \right) \quad (C.10b)$$

$$Z_n = \frac{2}{n \pi} \sin \left(\frac{n \pi a}{b} \right) \quad (C.10c)$$

From initial conditions

$$C(0,0,0,0) = C_B \quad (C.11)$$

and at $t = \infty$

$$C(0,0,0,\infty) = C_A \quad (C.12)$$

The solution is

$$C(x,y,z,t) = C_A + (C_B - C_A) C_1(x,y,z,t) \quad (C.13)$$

Appendix D

```

10 REM *****
20 REM
30 REM ANALYSIS OF MINIMUM CONCENTRATION OF BORON TO ALLOW
40 REM AMORPHIZATION TO OCCUR AND INHIBIT EPITAXIAL REGROWTH
50 REM OF FERRITE IN IRON-BORON ALLOYS WHEN LASER PROCESSED
60 REM WITH A NANOSECOND EXCIMER LASER
70 REM
80 REM AUTHOR: J.W. MCCAMY
90 REM
100 REM *****
110 REM
120 REM GSB.....BORIDE GRAIN SIZE IN ANGSTROMS
130 REM DIFC.....DIFFUSION COEFFICIENT
140 REM C.....BORON CONCENTRATION (AT%)
150 REM CS.....AT% BORON IN SAMPLE
160 REM WCS.....WT% BORON IN SAMPLE
170 REM WCB.....WT% BORON IN FE3B BORIDE
180 REM CA.....AT% OF BORON IN FERRITE
190 REM WCA.....WT% OF BORON IN FERRITE
200 REM T.....TIME IN SECONDS OF DIFFUSION
210 REM V.....VOLUME FRACTION OF CRYSTALLINE
220 REM MATERIAL IN SAMPLE (DETERMINED
230 REM EXPERIMENTALLY)
240 REM WCV.....WT% BORON AT CRY/AMORP BORDER
250 REM CV.....AT% BORON AT CRY/AMORP BORDER
260 REM
270 REM *****
280 REM
290 DIM B1(100)
300 V=.4
310 T=1.5E-07
320 GSB=5000
330 G=GSB/2
340 DIFC=1E+13
350 CA=0
360 CB=25
370 CS=10
380 WCA=CA/100*10.81/(CS/100*10.81+(1-CA/100)*55.85)
390 WCB=CB/100*10.81/(CB/100*10.81+(1-CB/100)*55.85)
400 WCS=CS/100*10.81/(CS/100*10.81+(1-CS/100)*55.85)
410 AB=((WCS-WCA)/(WCB-WCA))^3
420 B=G/AB
430 AC=((1-V)*B)^3
440 PI=3.14159
450 LAM=(PI/B)^2*DIFC*T
460 FOR I=1 TO 100
470 B1(I)=2*EXP(-I^2*LAM)/PI/I
480 IF B1(I)<1E-10 GOTO 500
490 NEXT I
500 LL=I-1
510 FOR I=1 TO LL
520 CX1=I*B1(I)*SIN(PI*I*AB)*COS(PI*I*AC/B)
530 NEXT I
540 WCV=WCA+(WCB-WCA)*(AB+CX1)^3
550 CV=55.85/(10.81/WCV+45.04)
560 PRINT "DIFFUSTION TIME =";T*1E+09;" (ns)"
570 PRINT:PRINT "MINIMUM WT% BORON FOR AMORPHIZATION= ";WCV*100
580 PRINT:PRINT "MINIMUM AT% BORON FOR AMORPHIZATION= ";CV*100
590 END

```

SAMPLE OUTPUT FROM PROGRAM

DIFFUSTION TIME = 150 (ns)

MINIMUM WT% BORON FOR AMORPHIZATION= 1.07309

MINIMUM AT% BORON FOR AMORPHIZATION= 5.30686

VITA

James W. McCamy was born in Florence, Alabama on February 10, 1959. He attended elementary school in that city and was graduated from Mars Hill Bible School in June 1977. He entered Auburn University in September of that year, and in June 1982 received a Bachelor of Science degree in Chemical Engineering.

After two years with Amoco Production Company, he and his bride moved to Knoxville, Tennessee where he entered the Graduate School of the University of Tennessee as a part-time student in September of 1984. In June of 1985 he accepted a teaching assistantship and began full-time study toward a Master of Science degree in Metallurgical Engineering. He received this degree in December 1987.

The author is a member of the American Institute of Chemical Engineers, The Metallurgical Society of AIME and Tau Beta Pi.

In April 1987 Mr. McCamy accepted an appointment from the Oak Ridge Associated Universities program, and will pursue a Doctor of Philosophy degree in Metallurgical Engineering at the University of Tennessee, Knoxville.