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Crystallization, embrittlement and fracture morphology of annealed $Fe_{81}B_{13.5}Si_{3.5}C_2$

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Crystallization of $Fe_{81}B_{13.5}Si_{3.5}C_2$ (Metglas 2605SC) was investigated using angular dispersive X-ray diffractometry and energy dispersive X-ray diffractometry. Transition temperatures were determined by annealing an array of specimens from 0 to 97 h at temperatures ranging from 140 to 490° C. Samples of Metglas 2605SC began to transform in about 2.2 h at 365° C. Crystallization temperatures and products were compared to those previously reported in the literature. In addition, the embrittlement behaviour of the alloy was investigated and the fracture topographies of the as-received and annealed samples were examined and categorized using scanning electron microscopy. The Metglas tended to embrittle easily within short periods of annealing at temperatures as low as 240° C.

1. Introduction

Metglas 2605SC is a successor to Allied Corporation's 2605S ($Fe_{82}B_{12}Si_6$) and 2605 ($Fe_{80}B_{20}$) and is considered to have a "superior combination of magnetic properties and economy of raw materials as compared to its predecessors" [1]. Power distribution transformers are the single largest potential marketing opportunity for amorphous metallic alloys, and it has been estimated that use of Metglas 2605SC in place of the Si–Fe presently utilized for such transformers would save the United States millions of dollars [2, 3]. Progress has been thwarted by the unavailability of wide sheets (about 16 cm) necessary for fabrication of the transformer [4] and other manufacturing problems [2]. Subsequent to this research Allied Corporation introduced 2605S2, a reversion to ternary FeBSi, in recognition of the instability problems with 2605SC.

Because of the emphasis on potential applications, studies on the crystallization and embrittlement behaviour of these metallic glasses are of practical as well as scientific interest. Two types of diffraction methods were employed by these authors to investigate the transformation process: angular dispersive and energy dispersive X-ray diffractometry, as well as scanning electron microscopy and embrittlement analysis.

2. Experimental procedure

The samples examined were Allied Metglas 2605SC with the specific composition of $Fe_{81}B_{13.5}Si_{3.5}C_2$. Original sample size received from Allied was 6 m length, 5 cm width with a nominal thickness of 25 μm.

Some samples were tested as received from Allied Corporation. Other specimens were annealed in an argon atmosphere furnace for times up to 97 h and at temperatures ranging from 140 to 490° C. Specimens were trimmed to approximately 2.54 cm wide and 10 cm long to fit the diffractometer mount. To assure reproducibility, they were marked with a diamond scribe and the mark was aligned with a point on the mount each time the specimens were replaced in the diffractometer unit. Energy dispersive X-ray diffractometry (EDXD) spectra were acquired from a minimum of four areas on each specimen annealed at the various times and temperatures. Angular dispersive X-ray diffractometry was performed to confirm the EDXD results and, in general, a minimum of four areas on each specimen annealed at each time–temperature combination were examined. For many time–temperature combinations, duplicate tests were conducted and it was noted that reproducibility was high.

Traditional angular dispersive diffractometry was performed using a General Electric SPG Goniometer, XRD–5 Diffraction Unit, and copper target X-ray tube, generally operated at 25 to 28 kV and 30 to 33 mA. The samples were scanned through angles of $2\theta = 35$ to 85° and analysed with Cu$K\alpha$ radiation, wavelength $\lambda = 0.154$ nm.

EDXD was performed utilizing the white radiation provided by a silver target X-ray tube. A General Electric XRD–5 Diffraction Unit acted as power source and the tube was generally operated at 25 to 28 kV and 10 to 33 mA. The detector, a Tracor X-ray Si(Li) Spectrometer with approximately 141 eV resolution, was mounted on a General Electric SPG Goniometer fixed at $2\theta = 30.26°$. Spectra were recorded utilizing a Tracor Northern TN2000 X-ray Analysis System. Spectra were generally recorded from 5 to 25 keV and for a present integral of 200 000 counts per spectrum.

Embrittlement states were determined by bending the specimens with a pair of tweezers. The ribbons which broke into several pieces during bending were designated brittle. Specimens which shattered during bending were considered very brittle [5]. Fracture

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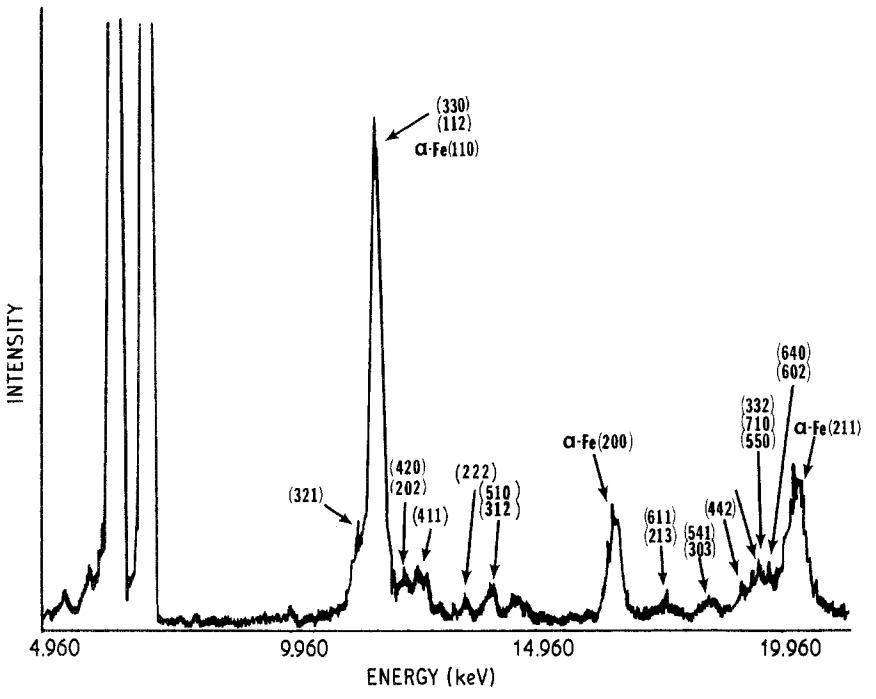

Figure 1 EDXD spectrum for Metglass 2605SC furnace annealed for 2 h at 420° C. Peaks are labelled with the appropriate Miller indices for both the α-Fe and Fe_3B tetragonal phases.

surfaces of the broken samples were analysed using an ISI–60A Scanning Electron Microscope.

3. Results and discussion

A published account [6] on the crystallization of 2605SC has indicated that the alloy initially crystallizes at 450° C as an α-Fe phase and with subsequent heating changes to an α-Fe phase plus an Fe_3B phase. Using angular dispersive X-ray methods, these investigators found that anneals of 3 h at 390° C, 30 min at 420° C or 5 min at 435° C caused addition of the α-Fe lines to the amorphous spectrum. After 3 h at 450° C the amorphous maximum was still evident, but after four more hours at the same temperature they determined that the pattern was largely crystalline and included the spectrum of Fe_3B. Prasad *et al.* [7] found that the phase transformation for 2605SC takes place gradually over a range of 477 to 537° C and that a sample heated in vacuum to 800° C and retained for 2 h at that temperature yielded X-ray and Mossbauer spectra with α-Fe and Fe_2B as the two major components.

The crystalline behaviour of furnace-annealed $Fe_{81}B_{13.5}Si_{3.5}C_2$ as observed by the present authors was as follows. After 2 h at 390° C, 2 h at 420° C or 1 h at 490° C the energy dispersive spectrum was largely crystalline, consisting of an α-Fe phase and an additional phase. This second phase concurred with the body-centred tetragonal Fe_3B structure determination of Walter *et al.* [8]. Coincidence of energy values with peaks in the spectrum of a sample annealed for 2 h at 420° C is shown in Fig. 1. The (*h k l*) Miller indices are labelled for both the α-Fe and Fe_3B phases. Because Fe_3B is considered metastable and the exact structure is uncertain [9, 10], the actual diffraction data obtained for this second phase were also compared with calculated energy values for an orthorhombic Fe_3B phase (a = 0.4454 nm, b = 0.5433 nm, c = 0.6656 nm) [9] and a tetragonal Fe_2B phase (a = 0.5099 nm, c = 0.4240 nm) [11]. No precise correlation was found between either of these phases and the unknown phase present in the energy dispersive spectra for annealed Metglas 2605SC.

Additional annealing experiments for 6 h at 420° C and to 26 h at 340° C yielded an energy spectrum consisting of a single α-Fe phase with some amorphous background present. This was confirmed utilizing angular dispersive diffractometry. The crystallization behaviour of furnace-annealed Allied Metglas 2605SC is summarized in the time–temperature transformation curve in Fig. 2. The phases present at each time and temperature combination are designated as

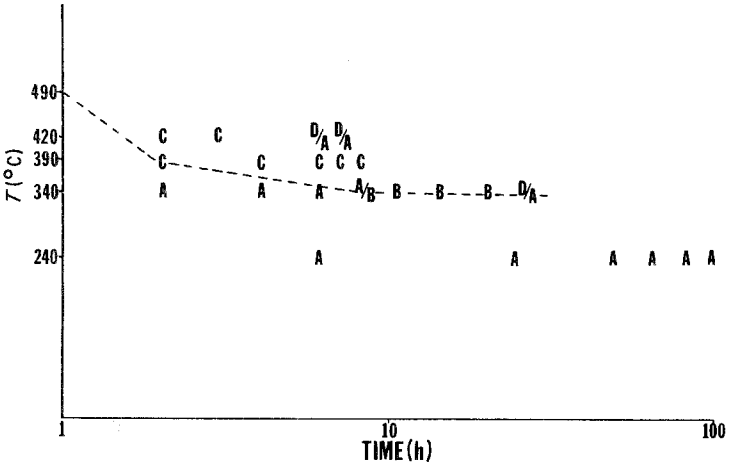

Figure 2 Time–temperature transformation curve for furnace-annealed Metglas 2605SC. A = amorphous, B = amorphous/crystalline, C = α-Fe + Fe_3B, D = α-Fe.

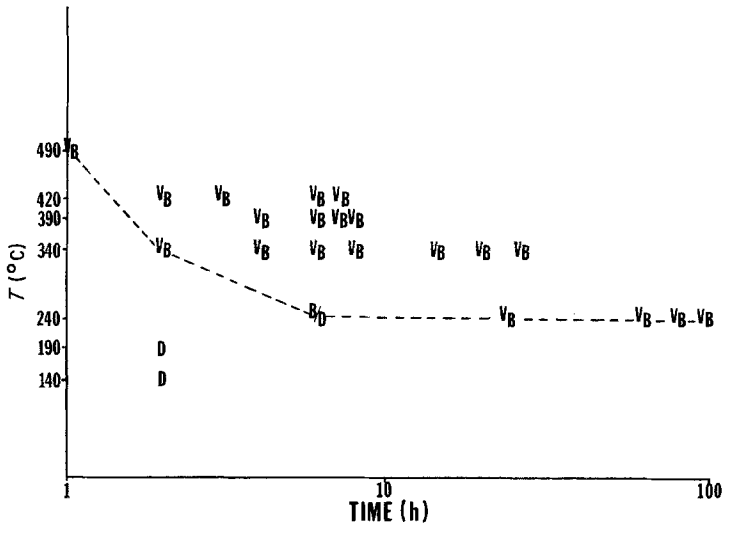

Figure 3 Time–temperature embrittlement curve for furnace-annealed Metglas 2605SC. D = ductile, B = brittle, VB = very brittle.

follows. The letter A indicates a totally amorphous spectrum and B designates a spectrum with some sharpening of peaks. The letter C represents a spectrum containing the phases α-Fe and Fe_3B, while D indicates a spectrum with only α-Fe present. Any combination of these letters designates a combination of phases with the first phase indicated being the predominant phase present in the spectrum.

Annealed samples of $Fe_{81}B_{13.5}Si_{3.5}C_2$ tend to be very brittle. A number of investigators have indicated that iron-containing glasses, in general, become brittle after annealing without crystallization, apparently as a result of structural relaxation [5, 12–16]. Simple iron alloy systems embrittle due to crystallization, but the kinetics of embrittlement in many amorphous metallic alloys do not correlate with the transformation process or with the rate of stress relief [5, 13, 17, 18]. The embrittlement temperature T_B has in the past been defined as the annealing temperature for approximately two hours, at which time the glass becomes brittle. T_B can differ by about 100 K from specimen to specimen, presumably due to different frozen-in structures at various rates of quenching [13].

Although the exact atomic nature of embrittlement in metallic glass is unknown, Chen [5, 13] has proposed that local structural and compositional variations, somewhat similar to phase separation, in the regions of 2 nm, accompanied by structural relaxation may lead to enhanced embrittlement. Resulting stress concentrations around the clusters may be responsible for the embrittlement. Observations in the ternary alloys, Fe–Co–P, Fe–P–Si and Fe–P–B demonstrate a greater tendency to become brittle and the corresponding binary alloys Co–P, Fe–P and Fe–B.

A graph of embrittlement with time and temperature for Metglas 2605SC appears in Fig. 3. Here, D indicates ductile; B, brittle; and VB, very brittle. In the as-received state, 2605SC is ductile, requiring numerous bends to break or tear. With minimal annealing (6 h at 240° C) it becomes embrittled, although a complete bend was needed to break the sample. The dotted line represents a conservative observation of the time necessary for embrittlement as a function of temperature. After only 2 h at 340° C the glass becomes very brittle. Chen [13] performed similar tests on 20 μm thick $Fe_{80}B_{20}$ and $Fe_{80}B_{17}Si_3$ ribbons prepared using a centrifugal spinning technique and annealed for 2 h. He reported the embrittlement temperatures, T_B and T_{VB} (very brittle), for $Fe_{80}B_{17}Si_3$ as 347 and 437° C, respectively. Davis *et al.* [15] found T_B for $Fe_{80}B_{20}$ (Metglas 2605), subjected to a two-hour anneal to be only 277° C, 100° C lower than Chen's value, while T_{VB} was the same as that of Chen.

The embrittlement curve for Metglas 2605SC is compared with the alloy's time–temperature transformation (TTT) curve in Fig. 4. The same specimens were used to construct both curves. The alloy became very brittle at times and temperatures well below those for which crystallization occurred.

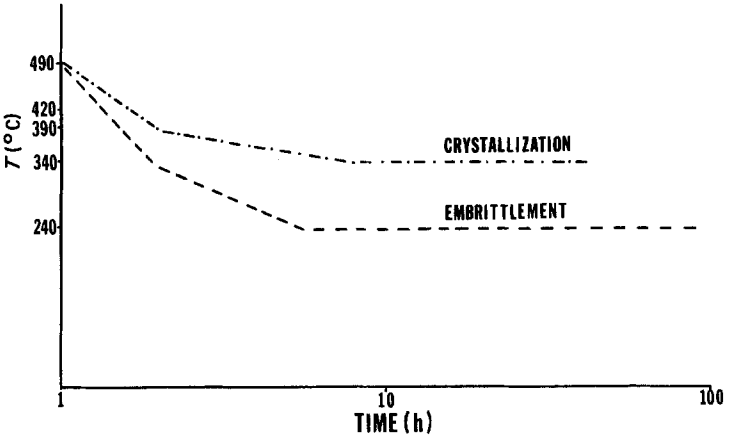

Figure 4 Overlap of embrittlement and transformation curves for furnace-annealed Metglas 2605SC.

To further correlate embrittlement behaviour with the transformation to a crystalline state, the fracture morphologies of the heat-treated 2605SC specimens were also analysed. Fracture topography has been investigated by a number of investigators for a variety of amorphous metallic alloys.

Chen and Wang [19], Masumoto and Maddin [20] and Leamy *et al.* [21] first noted that plastic flow in metallic glasses at temperatures below the glass transition temperature occurred in the form of localized shear deformation bands. Amorphous metallic alloys, deformed in tension, undergo localized shear in the direction of maximum shear stress and then fracture by decohesion within the locally deformed areas [21]. Two distinct modes are exhibited by the fracture surfaces: a smooth, essentially featureless zone produced by local plastic shear, and a veiny pattern of local necking protrusions formed during rupture and similar to that on fractured liquid adhesives. Leamy *et al.* [21] suggested that this pattern results from adiabatic heating created by plastic flow. This leads to localized deformation and eventual specimen failure producing the vein pattern. Spaepen and Turnbull [22] proposed that the fracture pattern is the result of the breaking of a fluid layer between two solid surfaces. The pseudo-cleavage mode was presented by Pampillo and Reimschuessel [23], who suggested that the concentrated shear deformation prior to failure defines a weaker "pseudo-cleavage" plane on which nucleation and propagation of cracks can occur easily. The ridges are formed when cracks, nucleated at various sites, coalesce. This mode has been identified on the fracture surfaces of a number of, but not all, the amorphous alloys studied [24].

The presence of the vein pattern is also strongly related to the method of macroscopic deformation. A glass that fails in tension by this mode may fail to produce the vein pattern when subjected to repeated sharp bending [25]. The absence of a vein pattern indicates that the external constraint must promote or allow the formation of a shear slip surface across the specimen in order to allow failure by this mode [24].

Changes in composition, temperature, and heat treatment vary the type of failure [24]. Often mixed fracture modes appear. In iron–nickel based alloys these include an essentially featureless topography, the discussed vein pattern, a dimpled rupture surface, and chevron markings [24, 26, 27]. The fracture morphology for samples of 2605SC was analysed by the present authors. Again, the samples were the same as those utilized for the investigation of the alloy's crystallization process. Much like the fracture morphology in iron–nickel based alloys, the fracture surfaces of $Fe_{81}B_{13.5}Si_{3.5}C_2$ ribbons displayed a wide range of modes. Fig. 5 exhibits scanning electron micrographs for the sequence of anneals at 390° C. These are representative of the fracture morphologies observed for other time–temperature combinations as well. All samples prior to annealing had similar fracture surfaces consisting of uneven ridging dotted with particles and cracks and, in some areas, a veiny pattern. After annealing, the fracture morphologies included dimpled rupture, ridging, fracture particles and chevron patterns.

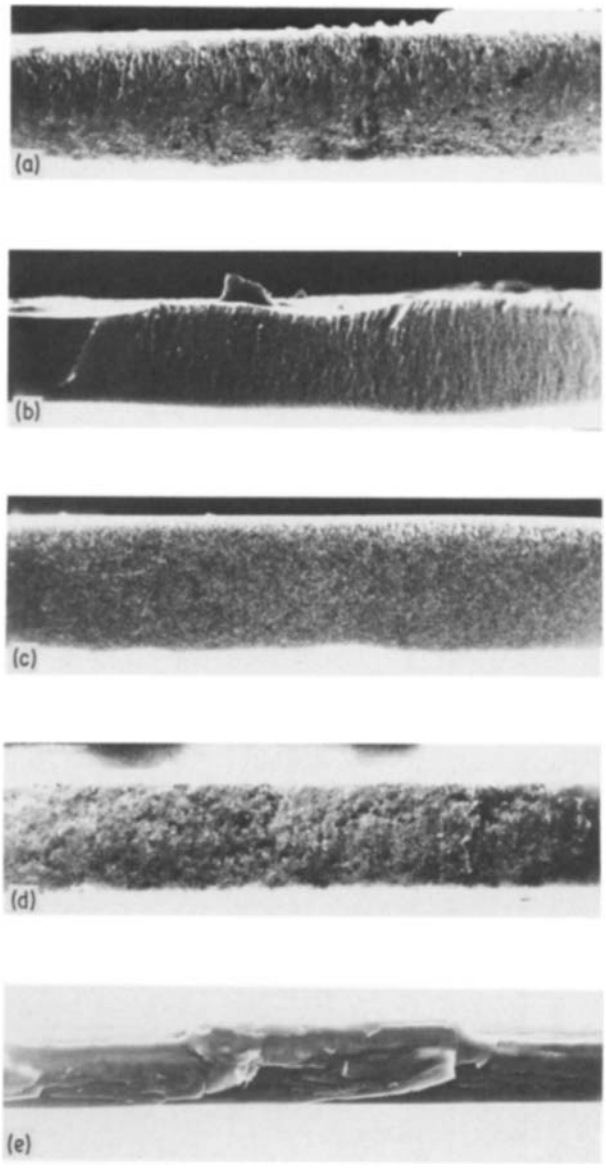

Figure 5 Representative scanning electron micrographs of the fracture surface of furnace-annealed Metglas 2605SC at 390° C (500 ×). (a) 8 h, (b) 7 h, (c) 6 h, (d) 4 h, (e) 0 h.

As indicated by the embrittlement curve and the fracture morphologies, Metglas 2605SC loses ductility after a minimum amount of annealing and at temperatures below the crystallization temperature. Comparisons with the corresponding X-ray data acquired do not provide a correlation between the onset of crystallization and embrittlement behaviour, although it has been suggested that heat treatment sufficient to cause embrittlement may cause, at most, traces of crystallization [15, 27, 28].

4. Conclusions

Annealing studies indicate that transformation to a crystalline state occurs after only 2 h at 390° C. Crystallization is also apparent following 26 h of heat treatment at 340° C. Minimal annealing of 6 h at 240° C causes Metglas 2605SC to become embrittled. After 2 h of heat treatment at 340° C, it becomes very brittle. There appears to be no correlation between embrittlement behaviour and the onset of crystallization at lower temperatures, although it may be speculated that fundamental experimental limitations

prevent such a correlation from being identified, i.e. that crystallites are in the process of formation at low temperatures, but their presence cannot be detected by energy dispersive or angular dispersive diffractometry. Analysis of the fracture topographies of the annealed samples coincides with that of the embrittlement behaviour but adds no new clues to the interaction of embrittlement with transformation behaviour. In a manner similar to the embrittlement tests the fracture surfaces of $Fe_{81}B_{13.5}Si_{3.5}C_2$ displayed a wide range of modes included dimpled rupture, chevron markings and vein patterns, and showed indication of embrittlement earlier than indicated by crystallization.

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