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Refractory-metal stabilized amorphous stainless steel

Part 2 *Effect of heavy ion irradiation on the crystallization behaviour*

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Concurrent heavy ion irradiation during annealing lowered the normal crystallization temperature and altered the type of crystallization reaction in an amorphous 304 stainless steel containing 14 at % tungsten. The crystallization temperature was lower by approximately 150 K during irradation and only a fine grained χ phase was formed during irradiation compared to the dual structure of b c c + χ phase formed in the absence of irradiation. The decrease in the crystallization temperature was attributed to radiation enhanced diffusion and the preferential formation of the χ phase was attributed to localized rearrangement of the amorphous structure due to displacement spikes.

1. Introduction

In Part 1 of this study [1], the high crystallization temperatures of amorphous stainless steel alloys were attributed to the complex structure of the crystallized phase. It is known that radiation affects both the rate of phase transformation and the types of phases formed in the crystalline alloys [2]. In the study reported here, heavy ion irradiation was found to have similar effects in transformations of an amorphous alloy. An understanding of radiation effects is important because the amorphous state is an important factor in surface modification techniques utilizing ion irradiation. The purpose of this investigation was to study the stability of a particular amorphous stainless steel alloy under irradiation with regard to its crystallization behaviour. The study utilized heavy ion bombardment for the irradiation and TEM for the microstructural analysis. The transformation under thermal annealing is first described. The crystalline transformation under irradiation is then compared to the thermal-anneal results. These results are discussed in terms of irradiation effects on atomic mobility and phase stability.

2. Experimental procedure

The amorphous alloy was prepared by high rate sputter deposition of 304 stainless steel and tungsten onto a cold substrate, as described previously [1]. The composition of the deposit used in this study was 61 at % Fe, 17 at % Cr, 8 at % Ni and 14 at % W and the thickness varied from 0.1 to 0.2 mm. Transmission electron microscopy (TEM) specimens approximately 3 mm in diameter were cut from the deposit and used for both irradiation and thermal annealing treatments.

The 3 mm disc specimens were thermally annealed for up to 48 h in the temperature range 675 to 975 K in a vacuum of 1×10^{-5} Pa. Both near-surface and interior regions of the sputter deposited material were examined by TEM in these specimens with no differences in crystallization behaviour detected between these regions. All specimen electropolishing for TEM examination was carried out after the annealing treatments.

For the irradiation treatment, the alloys were bombarded with 5 MeV Ni^{2+} ions at a current density of 1.6 $\mu A\,cm^{-2}$ and in a temperature range of 675 to 875 K. The vacuum during

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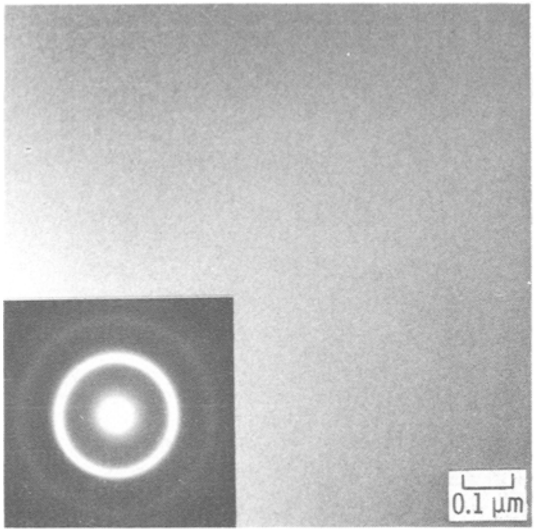

Figure 1 Microstructure of sputter deposited 304 SS + 14 at % W.

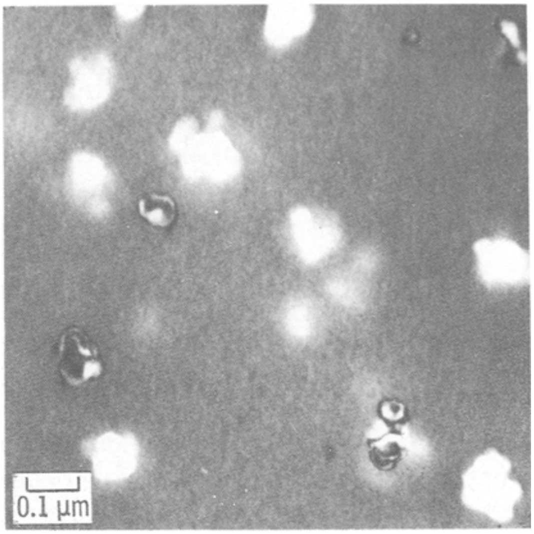

Figure 2 Microstructures of amorphous 304 SS + 14 at % W annealed 24 h at 775 K showing b c c phase formation.

irradiation was less than 1×10^{-6} Pa. Dose levels ranged from 0.16 to 20 displacements per atom (dpa) and the dose rate was approximately 5×10^{-3} dpa sec^{-1}. The damage was calculated using the approach of Manning and Mueller [3]. Specimens were selectively electropolished so that the TEM examination was made in a region approximately 500 nm from the bombarded surface. The damaged region extended to about 1.5 μm from the surface.

3. Results

The amorphous structure of the sputter deposited alloy was confirmed by both electron and X-ray diffraction. The diffuse diffraction rings and featureless microstructure, Fig. 1, are characteristic of amorphous alloys. The one strong diffuse ring and the two faint outer rings are similar to those observed in other sputter deposited amorphous alloys [4–6].

The transformation from an amorphous to crystalline structure during thermal annealing progressed from an iron-rich b c c phase, to a mixture of b c c and χ phase and finally to a mixture of f c c + χ phase. Crystals of a b c c phase formed in the amorphous alloy after a 24 h 775 K thermal anneal, see Fig. 2. The crystallization temperature, T_x, was approximately 920 K as measured by differential scanning calorimetry (DSC) but a lower T_x was noted when carrying out isothermal or isochronal anneals, as discussed in Part 1 [1]. The lattice parameter, calculated from electron diffraction patterns, of the b c c phase was 0.2870 nm ± 0.0005 nm which is close to that of α-Fe. The actual composition of the b c c phase could not be determined but an increase in magnetism indicated a high iron content. The kinetics of the amorphous to b c c transformation were very sluggish, and it is not known whether the crystallization of this phase was complete after annealing at 775 K for 48 h.

Crystals of a χ phase ($a = 0.8875$ nm) began to form in the remaining amorphous matrix at a higher annealing temperature at 875 K, see Fig. 3. The identity of the χ phase was based on the similarity of the crystal structure and lattice parameter to the known $Fe_{36}Cr_{18}Mo_{10}\chi$ phase. Molybdenum and tungsten behave similarly in iron alloys, so the phase is assumed to be $Fe_{36}Cr_{18}W_{10}$. Longer annealing times at 875 K produced a mixture of an f c c phase + χ phase, as shown in Fig. 4. Annealing for 48 h at 975 K produced a mixture of an f c c phase + χ phase. The lattice parameter of the f c c phase was close to that of γ-Fe.

In amorphous specimens irradiated at temperatures less than T_x, crystallization occurred at 675 K. This is about 150 K below that expected from thermal annealing for an equivalent time. Furthermore, the type and morphology of the crystalline phase was markedly different from that due to thermal anneals. An extremely fine grained χ phase formed throughout the irradiation zone; no b c c or f c c phase was observed, see Fig. 5.

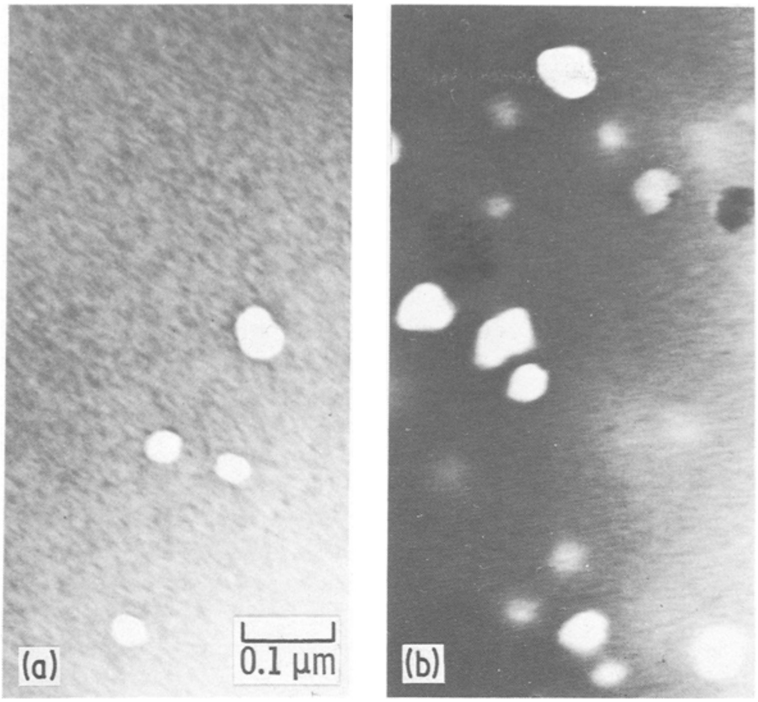

Figure 3 Microstructure of amorphous 304 SS + 14 at % W annealed at 875 K for (a) 0.5 h and (b) 1 h, showing b c c and χ phase formation.

The dose dependence of the onset of crystallization was a function of temperature. The crystalline phase was first noted after about 4 dpa at 675 K, but started forming after < 1 dpa at 775 K. The grain size was the order of 5 nm initially and appeared to saturate at 20 nm at high doses. The grain size was not a strong function of irradiation temperature.

The difference in the kinetics of crystallization due to irradiation is schematically shown in the time–temperature–transformation diagram, Fig. 6. The multi-step process for the non-irradiation

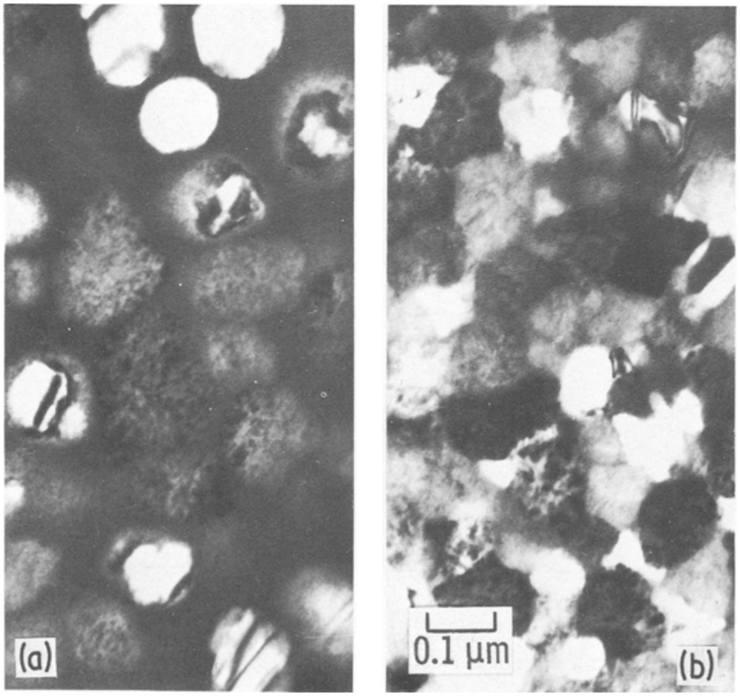

Figure 4 Microstructure of amorphous 304 SS + 14 at% W annealed 48 h at (a) 875 K showing b c c + χ phase and (b) 975 K showing f c c + χ phase.

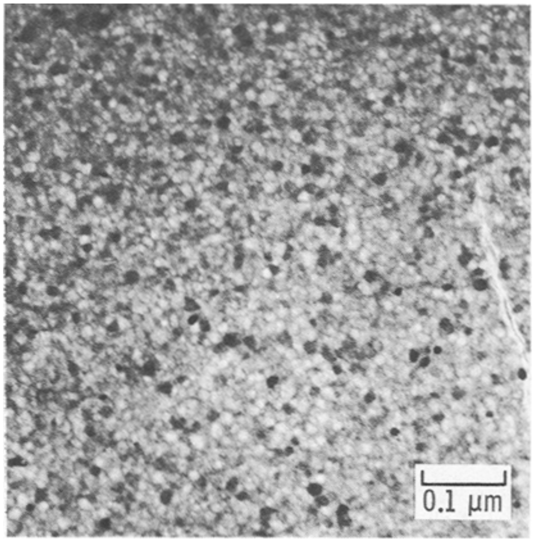

Figure 5 Amorphous 304 SS + 14 at W irradiated to 3 dpa (15 min) at 675 K showing fine grained χ phase.

transformation is similar to the crystallization behaviour reported for other amorphous alloys [7, 8]. The significant increase in the kinetics as a result of irradiation is shown by the shift of the transformation line to much shorter times. The transformation line for the irradiation case represents the minimum dose required for observable crystallization. There is undoubtedly a temperature below which the amorphous alloy will not crystallize, even under irradiation. Our results indicate it is at least less than 675 K.

The irradiation induced χ phase was relatively stable against subsequent thermal annealing. Thermal annealing at 825 to 875 K produced little observable change in structure. After 48 h at 825 K, isolated regions of the bcc and fcc crystals were observed, see Fig. 7. The crystals were very heterogeneously distributed and appeared to delineate some prior structure.

Ion bombardment of a thermally crystallized specimen, consisting of a mixture of bcc and χ phase, did not produce the fine grained χ phase. Some unidentifiable defect structure was produced, see Fig. 8, but there was no hint of a transformation to a fine grain χ phase even though the irradiation temperatures and times were equivalent to that used on the amorphous specimen. The fine grained χ phase is apparently unique to an irradiation induced amorphous to crystalline transformation.

4. Discussion

The lowering of the crystallization temperature

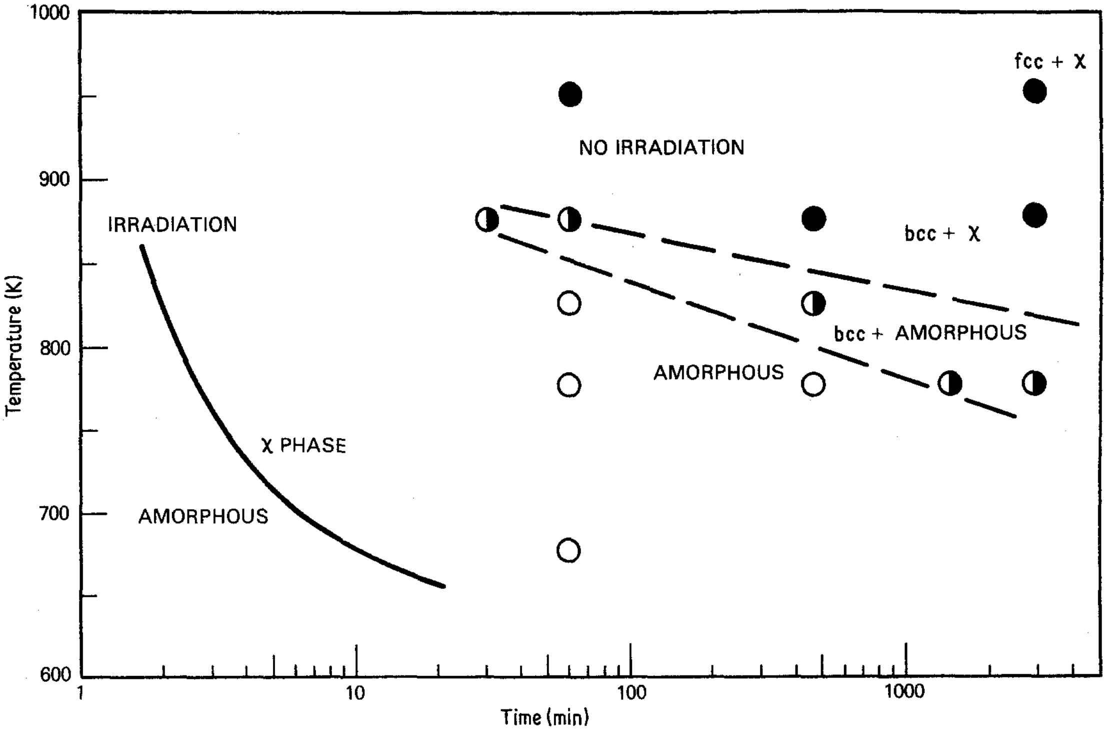

Figure 6 Time–temperature–transformation diagram for both irradiated and thermally annealed amorphous 304 SS + 14 at % W.

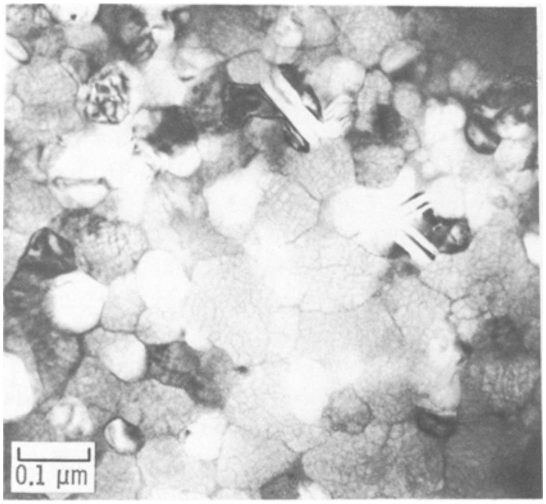

Figure 7 Microstructures of amorphous 304 SS + 14 at% W irradiated to 10 dpa at 725 K then annealed for 48 h at 825 K.

during irradiation agrees with the results of some previous studies on irradiation of sputter deposited, amorphous Mo–Ni [9]. An Fe–B type liquid quenched amorphous alloy also crystallized at a lower temperature during ion bombardment [10]. Light ion irradiation of amorphous carbon foils produced graphitization in a manner similar to a high temperature anneal [11]. Further, irradiation in a high energy electron microscope of amorphous Au–Si and Fe–C–B alloys resulted in a marked lowering of the crystallization temperature [12]. Radiation induced crystallization of amorphous ZrO_2 has also been reported [13] so the phenomenon appears to be of a general nature.

Radiation enhanced atomic mobility in the amorphous state can largely explain the increase in crystallization kinetics during irradiation. Diffusion processes in amorphous metals are not well defined but they do occur. The atomic displacements produced by the irradiation will increase the average excess free volume of the structure thereby leading to increased atomic mobility. The short-range atomic movements necessary for the crystalline form to develop are thereby assisted by the irradiation.

This behaviour of the amorphous alloys under irradiation is directly analogous to the effect of radiation on the order–disorder transformation [14, 15]. Irradiation causes a disordered alloy to become more ordered if the irradiation temperature is less than but close to the ordering temperature. At temperatures much below the ordering temperature, irradiation will cause more disorder because the displaced atoms can not move back to ordered sites. There is essentially a competition between ordering (due to enhanced point defect mobility) and disordering (due to displacement of atoms from their normal positions). The dominant process will be a function of temperature, dose rate, and the specific thermodynamic properties of the alloying elements. Apparently at temperatures as low as 150 K below the normal crystal-

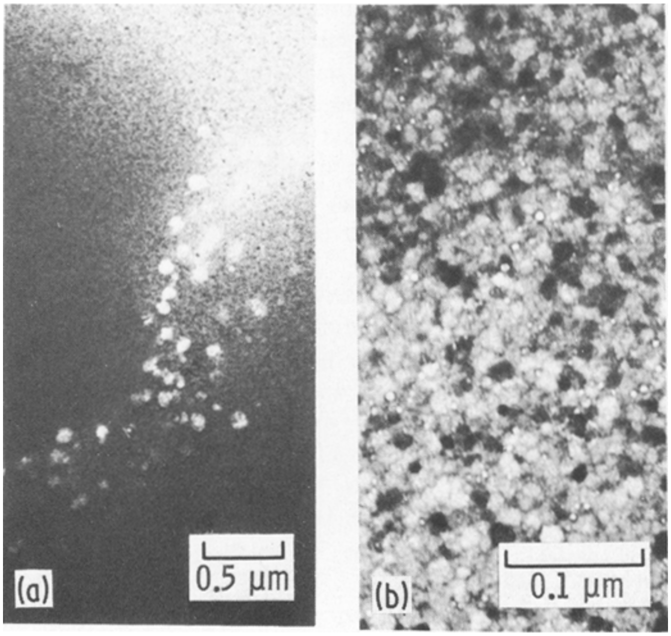

Figure 8 Microstructure of amorphous 304 SS + 14 at% W annealed 875 K for 1 h then irradiated to 10 dpa at 725 K (a) low magnification showing some b c c and f c c crystals (b) high magnification showing χ phase grains.

lization temperature, the irradiation enhanced atomic mobility is the dominant effect in these amorphous alloys.

The extremely fine grain size, $\leqslant 5$ nm, of the χ phase after radiation indicates a high nucleation rate and is evidence that the radiation enhanced, short-range atomic mobility or localized atomic rearrangement of the amorphous structure is the important factor. Also, if the radiation only changed the long-range diffusion coefficient, then the b c c phase should still be the first to form even during irradiation. Heavy ion irradiation produces significant displacement spikes and thermal spikes which result in localized regions of excess free volume. Rearrangement of short-range ordered clusters in the amorphous state into crystal nuclei would be easier in these spike regions. Behaviour is expected to be different during electron irradiation which produces only point defects and no spikes. Electron irradiation was reported to increase the crystallization kinetics but no mention of any change in the phase relationships or types of reaction was reported [12].

An explanation of the effect of the irradiation on the type of phase transformation is not clearly apparent but is likely to be related to changes in the activation energy of transformation for a particular crystalline phase. Intermediate phases form during crystallization because of the lower activation energy required to go to an intermediate phase as compared to a much higher activation energy required for direct transformation to the final equilibrium phase [16]. The b c c phase in the thermally annealed specimen represents a simple crystal structure and would be expected to have a low activation energy of formation. In many liquid-quenched amorphous iron alloys, a b c c α-iron type phase also initially precipitates. This type of crystallization is representative of a primary reaction in which a phase, rich in one of the principal alloying elements, first precipitates [8]. However, there is a compositional change between the crystal and the amorphous matrix in this type of reaction and, hence, some long-range motion is necessary. In contrast to the b c c phase, the χ phase is highly complex and has a relatively high activation energy for transformation. Consequently, it forms at higher temperatures during the thermal annealing.

It is proposed that, during irradiation, the induced atom movements reduce the activation barriers for transformation. The χ phase forms in preference to the b c c phase now because the χ phase can apparently accommodate all of the elements in its structure and only requires short-range atomic motion to do so. The nominal composition of the χ phase is 62 at% Fe, 21 at% Cr, 17 at% W, based on similarities to the Mo type χ phase. The measured composition of the alloy was 61 at% Fe, 17 at% Cr, 14 at% W, and 8 at% Ni, so only the nickel would have to be partitioned between the chromium and tungsten sites. The b c c phase can not accommodate all the elements so that solute rejection and long-range diffusion processes are still necessary for its formation even under irradiation.

The heavy ion radiation has therefore effectively changed the crystallization reaction from a primary type to a polymorphic type. In a polymorphous reaction, there is direct transformation to the final equilibrium phase with no compositional change. This reaction type has been observed in other amorphous alloys with a composition near an intermetallic compound [5].

5. Conclusion

The thermal crystallization of an amorphous 304 SS–14 at% W alloy proceeds by a primary reaction in a mixture of an iron-rich b c c phase plus an intermetallic χ phase. At higher crystallization temperatures and long times, a mixture of a f c c phase plus χ phase results. Concurrent ion bombardment during annealing lowers the crystallization temperature by at least 150 K and results in a polymorphous transformation to a fine grained structure consisting entirely of χ phase. The increase in crystallization kinetics is attributed to radiation enhanced short-range atomic mobility in the amorphous state. It is the very short-range atomic movements in a displacement spike that are most important in producing the χ phase in preference to the b c c phase during irradiation.

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