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STRUCTURE AND CRYSTALLIZATION OF Fe-Si AMORPHOUS THIN FILMS

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Résumé.- L'état amorphe et le processus de cristallisation de film amorphe de Fe-Si obtenus par évaporation sous vide ont été étudiés par spectroscopie Mössbauer, microscopie et diffraction électronique. Des spectres Mössbauer correspondant aux alliages amorphes ferromagnétiques $\text{Fe}_{50}\text{Si}_{50}$ et paramagnétique $\text{Fe}_{30}\text{Si}_{70}$ ont été obtenus par la technique en retour utilisant les électrons de conversion. Le large sextuplet obtenu à partir de $\text{Fe}_{50}\text{Si}_{50}$ comporte une structure fine qui ne peut être due à aucun composé connu; ceci suggère l'existence d'un ordre à courte distance dans les alliages fraîchement préparés. Par recuit, il apparaît des modifications de cet ordre à courte distance, bien avant la cristallisation qui a lieu à 250°C , avec d'abord l'apparition du sextuplet caractéristique de Fe_3Si_x suivi d'une composante de fer pure. Le recuit de l'alliage paramagnétique amorphe $\text{Fe}_{30}\text{Si}_{70}$ conduit progressivement à des cristaux de $\beta\text{-FeSi}_2$ de plus en plus parfaits.

Abstract.-Amorphous state and crystallization process of vacuum evaporated thin films of Fe-Si alloys were studied by means of Mössbauer spectroscopy, electron microscopy and electron diffraction. Mössbauer spectra from ferromagnetic amorphous $\text{Fe}_{50}\text{Si}_{50}$ and paramagnetic amorphous $\text{Fe}_{30}\text{Si}_{70}$ films were obtained with the back scattering method using the conversion electrons. In the typical broad sextet pattern from the $\text{Fe}_{50}\text{Si}_{50}$ film, a fine structure, which could not be attributed to any known chemical compounds or pure iron component, was observed, suggesting the existence of certain short range atomic configurations in the as deposited film. On the annealing, the change of short range order preceded the amorphous-crystalline transformation which took place at around 250°C . By further annealing, Fe_3Si sextets first appeared. It was then followed by the appearance of pure iron component that was one of the final products in the crystallization process. On the annealing of paramagnetic amorphous $\text{Fe}_{30}\text{Si}_{70}$, $\beta\text{-FeSi}_2$ compound with defective structure was formed, and it gradually became a nearby perfect $\beta\text{-FeSi}_2$ crystals by further annealings.

Many Mössbauer studies have been done on the crystalline state of Fe-Si alloys containing various iron silicides /1-4/, but few studies on the amorphous state and its crystallization process existed /5/. In the present study, the amorphous structure and crystallization process of vacuum evaporated thin films of $\text{Fe}_{50}\text{Si}_{50}$ and $\text{Fe}_{30}\text{Si}_{70}$ alloys were investigated by means of Mössbauer spectroscopy, electron microscopy, electron diffraction and electrical resistivity measurement. The thin films of Fe-Si alloys were deposited in an ultra-high vacuum system using an electron gun on pure aluminium foil, carbon film or mica plate depending upon the above different techniques. The Mössbauer spectra were obtained at room temperature with the back scattering method using the 7.3 keV conversion and 5.6 keV Auger electrons excited by the characteristic 14.4 keV γ -rays from ^{57}Co source in Cu. The specimen was directly attached to the electron counter of the Spijkerman gas flow type using the $\text{He}+6\text{pctC}_4\text{H}_{10}$ gas mixture. The resolution of this technique defined by the half width of resonance line was about 20% better than that of the ordinary transmission method.

A typical room temperature Mössbauer spectrum from ferromagnetic amorphous $\text{Fe}_{50}\text{Si}_{50}$ film and that

from paramagnetic amorphous $\text{Fe}_{30}\text{Si}_{70}$ film are shown in figure 1a and figure 2a respectively. The broad six line pattern with the maximum half width of 1.2 mm/s and the peak ratio, 3:4:1:1:4:3, of the former resembles to those of other ferromagnetic amorphous alloys, but there seems a fine structure especially in the outer most peaks. The spectrum is almost symmetric around zero Doppler velocity, i.e. with the isomer shift, 0.25 mm/s, relative to pure iron at room temperature. This value could be attributed to the expansion of atomic distances, less metallic band structure of the amorphous phase and/or solution alloying effect of Si. Fourier analysis taking account of the above peak ratio showed again a certain structure in a narrow spread of the internal field distribution, among which at least three components with the internal field of 180, 220 and 260 kOe respectively were noticeable but none of them corresponded to the known chemical compounds, Fe_3Si_3 , Fe_3Si , FeSi and others. This means that some sort of clusters with chemical interactions which, in ordinary conditions, do not exist as the equilibrium states might have been formed *in situ* in the deposited film. Another possibility is that the fine structure could arise from different near

neighbour configurations in the amorphous structure as would be expected in ordinary solid solution alloys.

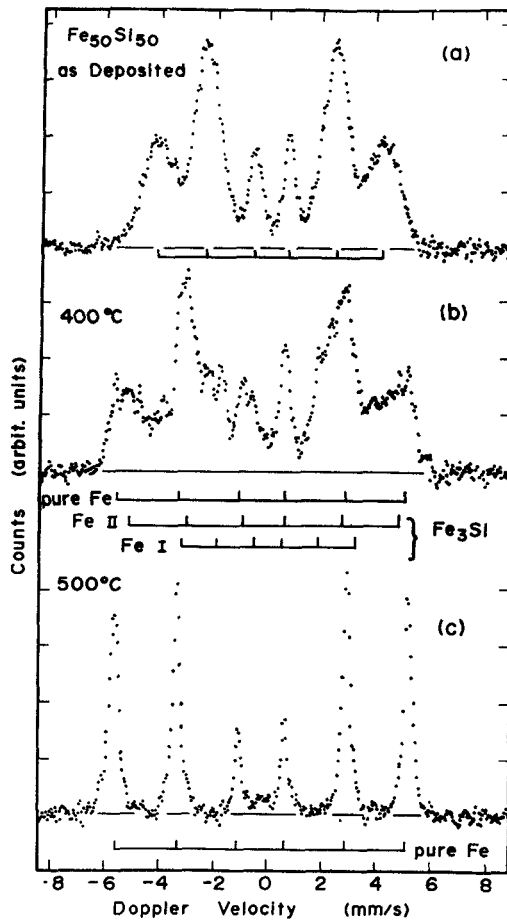


Fig. 1 : The Mössbauer spectra of $\text{Fe}_{50}\text{Si}_{50}$ film at room temperature. (a) as deposited -(b) after annealing at 400°C for 2 h. -(c) after annealing at 600°C for 2 h.

On the annealing below 200°C , the halo diffraction pattern and the structureless electron microscopical image of the amorphous $\text{Fe}_{50}\text{Si}_{50}$ film did not show any appreciable change, while in the Mössbauer spectrum some noticeable changes already occurred; the before mentioned fine structure became sharper and the spectrum moved to the larger internal field side by nine percent but no definite chemical structures were observed. This strongly suggests that variation of the short range order of the constituent atoms took place without any long range diffusion process. The Mössbauer spectrum by 200°C annealing had no pure iron component but two sets of internal field components corresponding to Fe_3Si and some unidentified peaks first appeared along with the main broad sextet with the internal field of about 280 kOe. At around 250°C , the film began to transform

to the crystalline state, exhibiting sharp diffraction lines corresponding to $\alpha\text{-Fe}$ and less remarkably those of Fe_3Si compound.

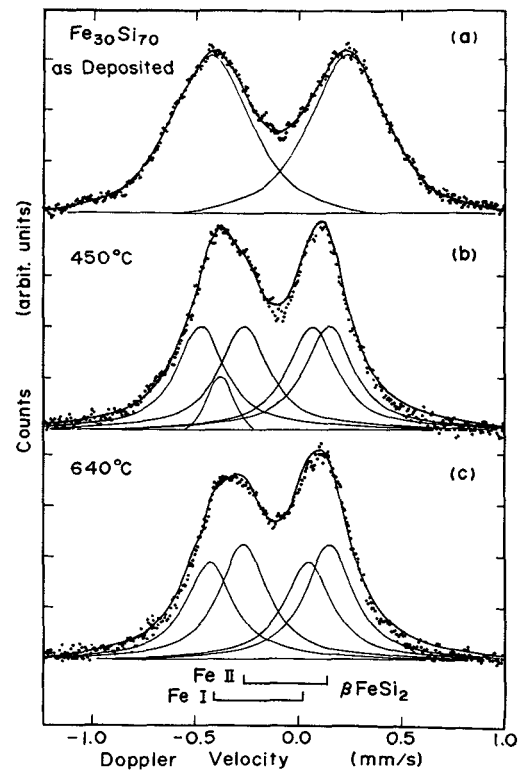


Fig. 2 : The Mössbauer spectra of $\text{Fe}_{30}\text{Si}_{70}$ film at room temperature. (a) as deposited -(b) after annealing at 450°C for 1 h. -(c) after annealing at 640°C for 1 h.

The electron microscopy revealed that in the crystallization process the nuclei of the crystallites were randomly formed in the amorphous phase and spherically grew until they became in contact with each other and finally covered the whole volume. The intensities of the diffraction lines of Fe_3Si and, in addition, those of Si increased by further annealing. In accordance with the changes observed by electron diffraction and microscopy, the Mössbauer spectrum showed Fe and Fe_3Si components above 250°C , which further grew at higher temperatures. An example of coexistence of pure Fe, Fe_3Si , and some unknown components on the annealing at 400°C is shown in figure 1b. On 500°C annealing, the crystallization and phase separation process were almost completed, and the Mössbauer spectrum nearly perfectly transformed to that of pure iron as figure 1c shows. A small central paramagnetic peak seems to arise from iron atoms dissolved in the silicon phase and line broadening around each peak may be attributed to the effect of Si in solution in pure iron lattice.

A large quadrupole split of about 0.6 mm/s and

broadness of the symmetrical doublet spectrum of the paramagnetic amorphous $\text{Fe}_{30}\text{Si}_{70}$ film presumably arises from the large electric field gradient induced by the asymmetrical and distorted atomic arrangements in the amorphous structure, which can be regarded as a super saturated high concentration solution. The good symmetry of the spectrum, as in figure 2a, indicates that the amorphous structure consists of unique phase with unique isomer shift without other chemical components with different values of the isomer shift. On the annealing of the amorphous $\text{Fe}_{30}\text{Si}_{70}$ film, the diffraction patterns and electron images changed at around 450°C , exhibiting the crystallization process with the emergence of $\beta\text{-FeSi}_2$ crystals of a complicated orthorhombic structure. In the Mössbauer spectrum an unmistakable change already appeared at around 350°C , and at 450°C it became sharper and asymmetrical, as figure 2b shows. The quadrupole split decreased to 0.5 mm/s at that temperature and by further annealing it reached to 0.4 mm/s in the average. The Mössbauer spectrum was able to be decomposed into two components with different quadrupole splits and isomer shifts as was expected in the bulk $\beta\text{-FeSi}_2$ crystal, in which two sorts of iron sites, I and II, associated by different Mössbauer parameters are contained /3/. In addition, at 450°C there existed a small unidentified single component at around -0.4 mm/s as in figure 2b, which became smaller and finally disappeared by the annealing at a higher temperature. The spectral analysis at various annealing stages also revealed that the quadrupole split of the Mössbauer component of iron at site II were invariant while that of site I decreased by the annealing. Even after the annealing at 640°C the site I component had a quadrupole split by 0.04 mm/s larger than that in the bulk $\beta\text{-FeSi}_2$. This means that site I is considerably defective after the amorphous-crystalline transformation.

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