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Structure and thermal stability of vapour-deposited Fe-Cu alloys

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The structure of vapour-deposited Fe–Cu alloys was analysed and compared with that obtained by quenching from the liquid and solid state. Transmission electron microscopy was used to observe grain size at room temperature and precipitation at elevated temperatures. A discussion of thermal stability of metastable phases is based on nucleation mechanisms and diffusion coefficients in the highly defect or glassy state and the crystalline state.

1. Introduction

The amount of copper that can be obtained in a bcc supersaturated homogeneous solid solution, depends on the production process (Fig. 1). It increases in the following sequence [1]:

(1) quenching from the temperature of maximum solubility in the α-solid solution,

(2) martensitic transformation of the γ-phase,

(3) quenching from the homogeneous liquid,

(4) vapour-deposition.

Up to about 10% Cu can be obtained in bcc solid solution by splat-cooling [1] and 50% by vapour-deposition [2], while the maximum solubility in equilibrium is only 2%. If the metals are deposited at room temperature, no amorphous phase is found in the whole range of Fe–Cu alloys. Iron–metalloid glasses like Fe–B and Fe–C can preserve a glass structure far above room temperature [3]. The homogeneous supersaturated α-Fe–Cu solid solutions may have originated from a homogeneous glass structure, the low crystallization temperatures indicating that this reaction takes place by individual atomic jumps as no decomposition which requires long range diffusion occurs (see Figs. 5 and 6). Magnetic properties [2, 4, 5] and electrical resistivity [6] of metastable Fe-, Co-, Ni-alloys obtained by vapour-deposition or splat-cooling were studied recently. A few structural investigations have been done by Mössbauer spectroscopy [7], X-ray and electron diffraction [1, 2], and electron microscopy [1]. Microscopic investigations of the solid state reactions are known from splat-cooled Fe–Ni [8] and Fe–Cu [1]. In Fe–Ni the martensitic transformation of the metastable phase was studied and precipitation of a fcc Cu-rich phase in Fe–Cu [9]. It is the purpose of this paper to analyse the structure and the annealing behaviour of Fe–Cu bcc solid solutions of extremely high supersaturation as produced by vapour-deposition.

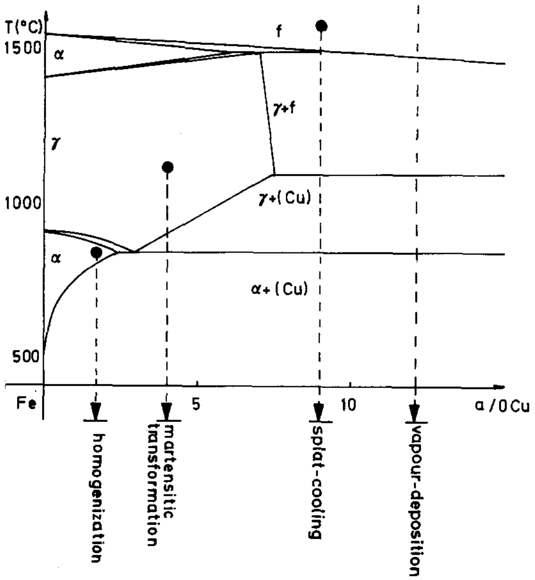

Figure 1 Fe–Cu phase diagram indicating the different methods for the production of supersaturated α-Fe–Cu solid solutions.

2. Experimental methods and results

Alloy of iron with up to 50 at.% Cu were produced by vapour-deposition at 20° C on NaCl substrates.

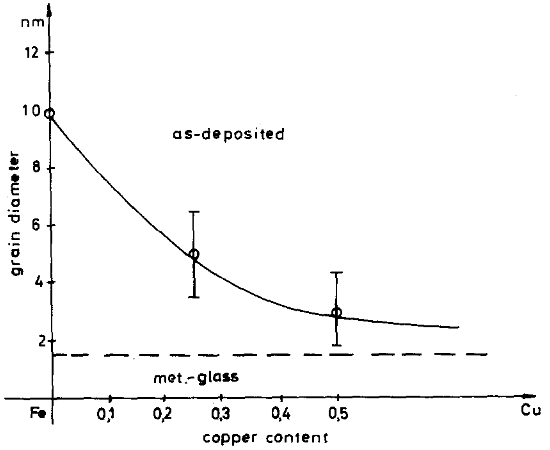

Figure 2 Average grain size of as-deposited α-Fe–Cu solid solutions.

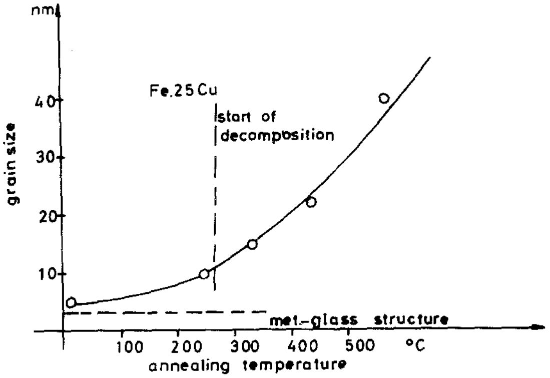

Figure 3 Crystallite size of Fe– 25 at. % Cu alloy after isochronal heating to 550° C.

In most cases homogeneous bcc solid solutions could be obtained up to this composition while $\alpha + \gamma$-phase mixtures were found at higher Cu-contents. The following compositions were investigated: Fe + 0, 15, 25, and 50% Cu. The compositions were determined from the ratio of Fe to Cu deposited, after annealing above 500° C from the volume portions of the phases. The accuracy is not better than ± 5%. The films were produced in a vacuum of 8×10^{-7} to 1×10^{-6} Pa from 99.96% Fe and 99.99%. Cu. The thickness of the films was about 50 nm.

Homogeneity and crystal structures formed after deposition during heat treatment were determined by selected area electron diffraction. Bright and dark field electron microscopy was used to determine crystallite sizes and the distribution of the newly formed phases. The heating stage of the Philips EM 300 was used to heat the films inside the microscope to temperatures up to 830° C in a vacuum of 10^{-2} Pa. This vacuum was was not sufficient to avoid oxidation while heating above 400° C inside the electron microscope. The vacuum of 10^{-5} Pa in the JEOL 200kV microscope, however, did not improve the results in this respect.

In the deposited condition at room temperature, all the alloys were extremely fine-grained bcc solid solutions (Fig. 2). The grain size decreased with increasing copper content and was always less than 10 nm (Figs. 3 and 4). The crystal structure of the alloys remained as bcc up to 250° C, as indicated by the diffraction patterns (Fig. 4). Moderate grain growth started below this temperature, indicated by decreasing line broadening of the electron diffraction rings. Grain size was determined by dark field images of a portion of the diffraction rings (Figs. 2 to 4).

The annealing behaviour was investigated by stepwise heating to 130, 250, 350, 450, and 830° C for 3 min at each temperature. Above 250° C new rings appear in the electron diffraction pattern and moderate grain growth continues. The ratio of the intensity of the rings of the bcc phase corresponds to that expected from the composition (Fig. 4).

The grain size of the two phases can be identified by dark field electron microscopy. In the Fe + 50% Cu alloy a duplex $\alpha + \gamma$-structure forms, while at smaller copper contents a transition from duplex structure to a dispersion is found. In the vapour-deposited films the dispersion is controlled by heterogeneous nucleation at the grain boundaries of fine-grained matrix. Additional metastable phases were not detected by electron diffraction during the decomposition process. Simultaneously with the reflections of the newly formed γ-phase, additional rings were found which could be identified as Fe_3O_4. This phase must have formed at the surface of the films as fine grains with random orientation.

3. Discussion

The ultra-fine-grained structure which was found in all Fe–Cu alloys deposited at room temperature is markedly different from the structure that forms during crystallization of covalently-bonded glasses such as Ge and Si, and of polymer glasses. The ultra-fine-grained structure indicates that nuclei for crystallization are copious in a metallic

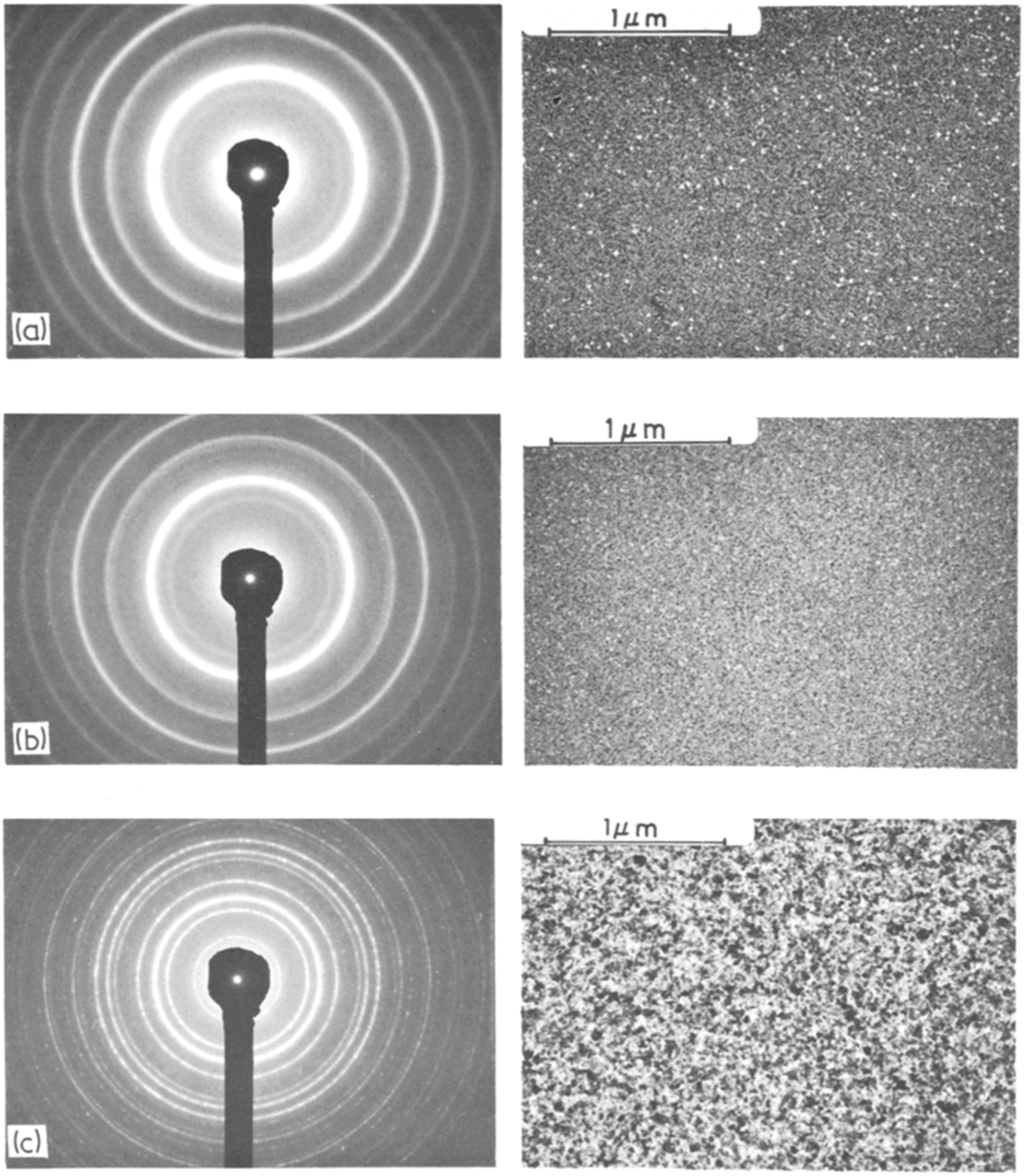

Figure 4 Transmission electron micrograph of the thin films Fe + 25% Cu. (a) as-deposited, (b) 3 min at 250° C, (c) 3 min at 440° C (in addition to γ-reflections, those of Fe_3O_4 appear due to contamination during heating in the microscope).

glass. Non-metallic glasses usually crystallize by the formation of polycrystalline spherulites due to the fact that nucleation sites are rare. Crystallization behaviour and therefore thermal stability of metallic and covalent glasses is qualitatively different.

The understanding of the structure of the Fe–Cu alloys can be based on a general survey of the reactions by which an amorphous solid can approach thermodynamic equilibrium (Fig. 5).

I transition of a less perfect to a more perfect glass structure (for example random network)
II glass A–glass B decomposition
III polymorphous crystallization
IV primary crystallization
V eutectic crystallization.

For purely metallic systems reaction I will take place immediately after deposition because of the undirectional nature of the bonds. During

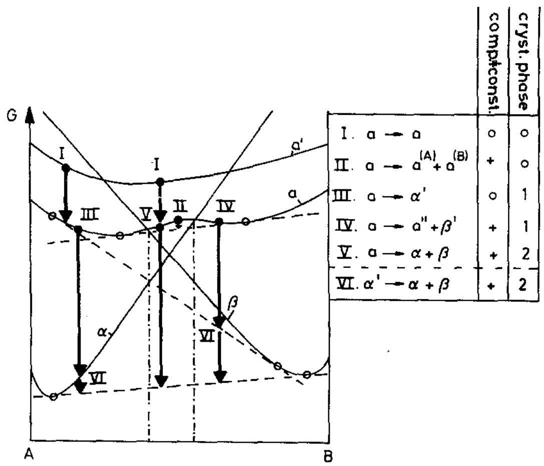

Figure 5 General survey of the reactions that can occur in a diatomic glass in a system with a simple miscibility gap. I transition in the glass structures, II glass–glass decomposition, III crystallization without change in composition, IV primary crystallization, VI secondary precipitation reactions.

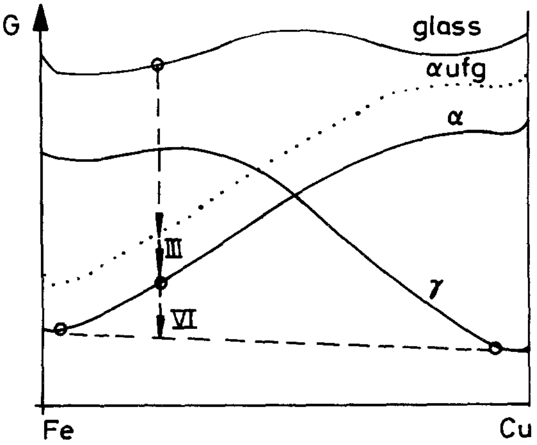

Figure 6 Special situation in Fe–Cu alloys: crystallization leads to an ultra-fine-grained solid solution (α_{ufg}) in which grain growth ($\alpha_{\text{ufg}} \to \alpha$) and precipitation ($\to \alpha + \gamma$) occurs.

deposition at room temperature reaction II and not reaction IV (which requires long range diffusion) occurs in metals (Fig. 6). In covalent glasses reaction IV is observed frequently in addition to all the other mechanisms if nucleation sites are rare, but long range diffusion is possible.

The exclusive formation of supersaturated α-phase in iron-rich alloys can be explained if the activation energy for nucleation of crystals is small (approximately zero) and the reaction rate is controlled by single atomic jumps at an activation energy for diffusion much less than that for substitutional elements in α-iron (Figs. 7 and 8). If a metallic glass structure provides structural units which can grow spontaneously during heating the ultra-fine-grain structure of about 2 nm observed at room temperature can be explained (Figs. 3 and 4). Discontinuous growth, such as in spherulitic crystallization or secondary recrystallization, must be excluded as it would not explain the grain shape and grain size distribution found (Fig. 4). As the process III of polymorphous crystallization is not associated with decomposition, it can take place by single atomic jumps from the defect as deposited to the ultra-fine-grain structure. If $Q_D \leqslant 100\,\text{kJ mol}^{-1}$ is the effective activation energy for diffusion in the glass, crystallization can take place below room temperature (Fig. 8). The secondary reaction VI must take place by long range diffusion in crystals or at grain boundaries (Figs. 7c and d). According to Fig. 8 this reaction should occur at $T > 300°\,\text{C}$, as was observed (Fig. 4). Depending on the volume proportion of the precipitation γ-phase, a dispersion (Fig. 7c) or a duplex structue (Fig. 7d) forms after reaction VI is completed. The only subsequent reaction is the annealing-out of grain boundaries and phase boundaries by continuous crystallite growth. The

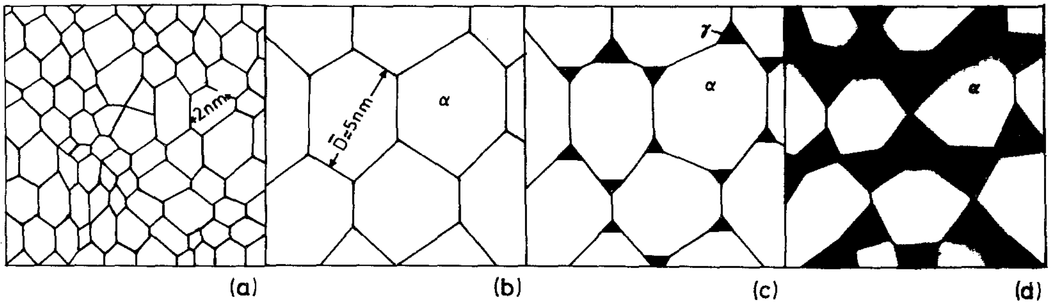

Figure 7 Schematic representation of the microstructures that were found in highly supersaturated Fe–Cu alloys solutions during heating; (a) ultra-fine-grained structure, as-deposited, (b) after grain growth at T < 250° C, (c) nucleation of copper-rich γ, 250° C < T < 350° C, (d) α + γ duplex structure, T > 350° C.

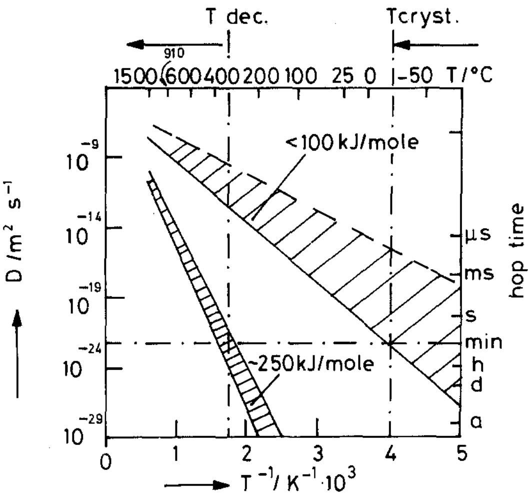

Figure 8 Temperature dependence of the diffusion coefficient of substitutional elements in iron: α-iron crystals $Q_D \approx 250\,\text{J mol}^{-1}$, iron glass $Q_D \leqslant 100\,\text{J mol}^{-1}$. The temperature ranges of crystallization and decomposition have been indicated.

major difference between vapour-deposited and splat-cooled Fe–Cu alloys is the much larger grain size of the latter. In these large grains homogeneous nucleation of f c c copper-rich particles starts above 400° C [1, 9]. The crystallization behaviour of the vapour-deposited films can be explained best by assuming that during deposition a transition from the structure of the metallic glass to an ultra-fine polycrystal with an average grain size of about 1 nm occurs. This transition takes place spontaneously due to the large number of defects in the crystallites. The crystallization process should then be identical to the annealing-out of these defects and rearrangement of the diffuse high-energy grain boundaries which had been formed during deposition into grain boundary structures of lower energy and higher coincidence.

4. Summary

Iron–copper alloys with up to 50% Cu have been produced by vapour-deposition at room temperature. The structure of the as-deposited films and their annealing behaviour up to 800° C were investigated using an electron microscope. Crystallization, grain growth and decomposition in this simple metallic system have been discussed.

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