

Classification
Physics Abstracts
66.30Ny — 81.40Ef

Electron Microscopy Investigation on the Effect of Plastic Deformation in the Alloying of the Immiscible System Cu-Fe

Massimo Angiolini, Francesco Cardellini, Marek Krasnowski(*), Giorgio Mazzone, Amella Montone and Marco Vittori-Antisari

ENEA, C.R. Casaccia. INN-NUMA, C.P. 2400, 00100 Roma, Italy

(Received April 7; accepted June 7, 1995)

Abstract. — The first steps of the solid state reaction between Cu and Fe induced by plastic deformation at low temperature have been studied by Transmission Electron Microscopy (TEM), X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC). Despite the positive enthalpy of mixing, plastic deformation induces interdiffusion in this system as evidenced by XRD and DSC analysis. TEM observations of samples prepared in different ways show the presence of some Fe into the Cu matrix, a relatively low density of dislocations, a large concentration of small agglomerates of point defects and a well-defined grain shape, suggesting that some dynamic recrystallization occurs during deformation. Considering the low processing temperature we advance the hypothesis that the excess concentration of point defects induced by the high strain rate plastic deformation can provide the necessary atomic mobility. Moreover the role played by these defects on the thermodynamic driving force of the alloying process is considered.

Introduction

The preparation of alloys by solid state reactions induced by plastic deformation has been extensively investigated in the last years, mainly by high energy ball milling of elemental powders [1]. The extensive plastic deformation imparted to the particles by the collisions leads to repeated cold welding and fracture, so that in the first step of the process a finely spaced multilayer of the starting elements is formed, with a periodicity generally decreasing with processing time. Later on, codeformation assists the interdiffusion process so that a true solid state alloying occurs despite the relatively low temperature [1].

As an alternative this kind of phenomena can be studied by repeated cold rolling [2] and controlled deformation [3] of artificial multilayers prepared by alternated stacking of foils of different elements. The reaction products are strongly dependent on the thermodynamic and transport properties of the elements relative to each other, as well as on the processing parameters; moreover also the presence of contaminating agents whose concentration is not always negligible can

(*) *Permanent address:* Institute of Atomic Energy, Swierk-Otwock, 05-400 Poland

play a role on the reaction path and on the final product [4]. The resulting phase or mixture of phases can represent both a stable or a metastable thermodynamic situation. For suitable elemental couples and processing parameters the reaction product can be a metastable amorphous alloy with structure and properties similar to what can be obtained by rapid quenching from the melt.

Even if the details of the solid state reactions occurring in these processes are not completely understood, it is often reported that the codeformation process seems to enhance the reaction rate and to give rise to unusual reaction paths, owing mainly to the fact that some phases present in the phase diagram are not able to nucleate in these experimental conditions [1]. However, in most cases the final product has a lower free energy than the starting mixture, so that the main task is to describe the reaction kinetics on the basis of a suitable metastable phase diagrams.

A few years ago it has been shown [5] that even elements which are almost immiscible in the solid state because of their positive enthalpy of mixing, like Cu-Fe, can be alloyed with the above method. Several hypotheses have been advanced in order to explain this effect mainly pointing to a thermodynamic justification for the driving force of the reaction, but up to now there is no unanimously accepted explanation. To this purpose, several details of the sample microstructure whose nature can, in principle, affect the relative free energies of the relevant phases have been taken into account. Eckert [6] has pointed out that the high dislocation density induced by the plastic deformation can increase the free energy of the starting Cu-Fe mixture, while Bormann [7], discussing the similar case of the Co-Cu system, has taken into account the contribution of the high density of interfaces to the enthalpy of the system. However it has been shown by Bormann [7] that the contribution of the dislocations is negligible in both systems owing to the fact that the atomic sizes of the elements are quite close to each other so that the segregation at the dislocations cores does not affect significantly their strain field and the stored energy. On the other hand the estimates made by the same author on the contribution of the interfaces show that periodicities typical of the usually hindered wavelengths in the spinodal decomposition and therefore of the order of a few nm are required to enhance the free energy above the metastable CuFe solid solution. Alternatively Yavary [8, 9] considered both the effect of possible oxygen contamination in the process and the enhanced solubility related to the Gibbs-Thompson effect making the hypothesis that Cu-Fe interfaces with a radius of curvature of the order of a few tens of nm can derive from the fragmentation of the starting powders in the ball milling process.

Most of the experimental work on this effect has been carried out by XRD, Mossbauer spectroscopy and DSC; the purpose of this paper is to investigate this effect by a careful investigation of the microstructure by TEM.

Experimental Method

Mechanically alloyed powders were obtained by milling in an Ar atmosphere in a Spex 8000 mixer-mill the equiatomic mixture of commercially pure 99.8% Cu and 99.5% Fe powders from Koch Chemicals. The mill was equipped with 2 balls of 12.7 mm diameter and the ball to powder ratio was about 5 to 1; moreover the milling vial was air cooled during the process.

Specimens for TEM observations have been prepared by embedding the powders milled for 1 h in an Al matrix with the following procedure. A small amount of powder was placed between two Al foils about 0.5 mm thick and this composite was plastically deformed in a hydraulic press up to cold-welding of the Al foils. Since this method can in principle affect the powder microstructure, even if this effect is not expected to have an important role owing to the severe plastic deformation experienced by the powders during the milling process and to the noticeable difference in mechanical properties between the powder itself and the Al matrix, some specimens have been

also prepared by embedding the powders in an epoxy resin. For both kinds of samples 3 mm discs could be punched after suitable mechanical grinding. Further sample preparation has been performed by dimpling, while final thinning was performed by Ar ion beam milling on a liquid N₂ cooled stage.

With the purpose of checking the effect of plastic deformation at high strain rate on the interdiffusion behaviour and on the material microstructure we have prepared also a second set of specimens by compressive deformation of trilayers prepared by inserting a 1.5 mm thick Cu sheet between two iron sheets about 2 mm thick with a procedure previously reported [10]. The trilayer surface area before deformation was about 0.25 cm². The deformation experiments were carried out with a hydraulic press with a maximum load of 250 KN applied in 0.1 s at temperatures ranging between room temperature and 500 °C. The trilayer thickness after deformation was about 1 mm so that an average strain rate of about 17 s⁻¹ can be estimated for this kind of samples. In this case thin foils for TEM observations were prepared in cross sectional geometry by mechanical methods followed by ion beam milling with a procedure already reported [10].

Observations have been carried out with a Jeol 4000 FX transmission electron microscope equipped with analytical facilities.

The microstructure and the thermal properties after different milling times have been also studied by XRD and DSC.

Experimental Results

Our XRD and DSC data are in good agreement with previously reported results. At the concentration under study, after milling for a sufficient time, the X-ray diffraction spectrum shows a single phase fcc structure with a lattice parameter slightly larger than that of pure Cu since the reflections of bcc Fe gradually vanish during the process. The DSC of a fully alloyed sample, shows the expected behaviour, with a quite broad exothermic peak extending from about 500 K to 900 K. After heat treatment at 973 K the X-ray diffraction pattern shows again the presence of both fcc Cu and bcc Fe.

Since our purpose is to study the first stages of the alloying process, we have observed by TEM the powder milled for 1 h. The results can be summarized as follows.

At the first stages of milling the powder is strongly inhomogeneous since the stochastic nature of the process gives rise to different histories for different powder particles. In particular, if the sample is examined by experimental methods with high spatial resolution several local situations can be observed which can be significantly different to each other. In addition to several spots where the unreacted elements are present, some alloyed grains can be found. Figure 1 shows the dark field image of an fcc grain with a Fe concentration of about 12% measured by X-ray microanalysis. The microdiffraction pattern evidences a single crystal fcc structure, so that we can exclude the presence of overlapping grains contributing to the X-ray signal. In general the microstructure shows the presence of a relatively small density of extended defects and in the larger Cu-rich grains some twins can be observed, suggesting that some sort of dynamical recrystallization occurs during the process. In fact this behaviour is observed also in relatively large grains so that it cannot be ascribed to the small grain size where the dislocation multiplication mechanisms can be hindered. In some Cu-rich areas extra spots can be observed in the selected area diffraction pattern, which can be indexed as belonging to the Cu₂O phase (Fig. 2). Dark field images obtained with these reflections show often a homogeneous distribution of small particles which appear to have precipitated in the fcc matrix. Notice that the sample was inserted into the microscope just after the ion milling process so that surface oxidation is not expected to be responsible for this feature. Moreover the presence of oxide particles was detected only in some grains.

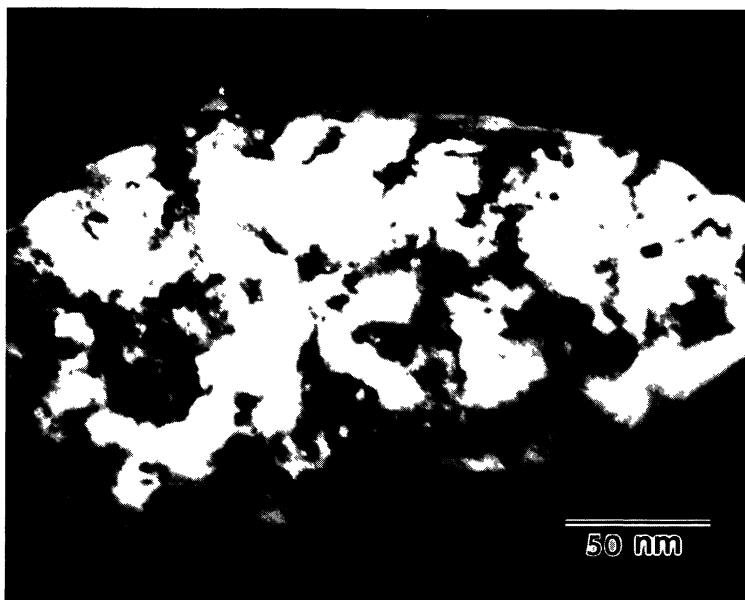


Fig. 1. — Dark field image of a fcc grain with 12% Fe content in the sample mechanically alloyed for 1 h.

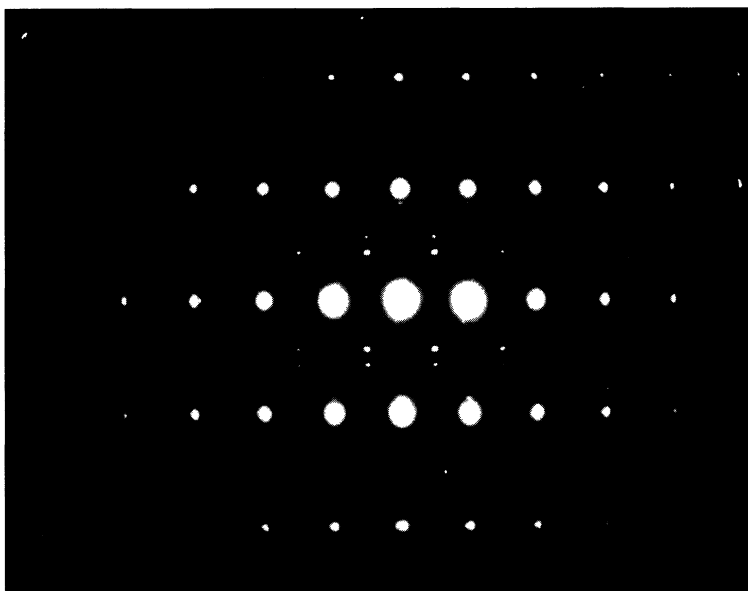


Fig. 2. — Selected area diffraction pattern from a Cu-rich grain in the sample mechanically alloyed for 1 h.

In Figure 3 where an out of focus image of a Cu-rich area is reported, it is possible to observe the presence of a high density of small intragranular voids with a relatively homogeneous distribution.

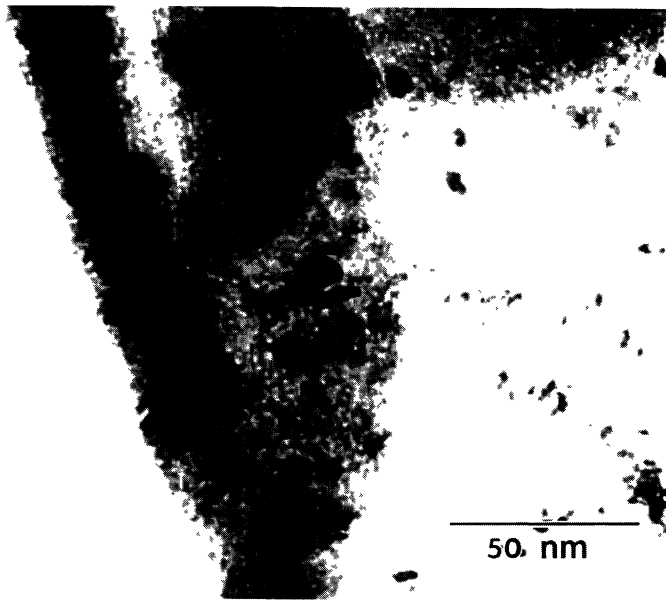


Fig. 3. — Out of focus image of a Cu-rich area in the sample mechanically alloyed for 1 h.

Summarizing, despite the noticeable inhomogeneity of the sample, it is possible to say that the observed microstructure is characterized by the presence of some alloyed grains, of a large density of small voids, of Cu_2O precipitates which show a definite orientation relationship with the matrix and by a relatively low amount of extended defects.

As far as the second type of samples is concerned, we obtained bonding between Cu and Fe only for processing temperatures higher than 300°C .

The typical microstructure of the Cu grains is shown in the weak beam image of Figure 4 and it appears to be the same for all deformation temperatures. While many annealing twins are present, the grain size is of the order of several μm . The dislocation density is relatively low and a large density of small defect clusters can be observed. Also in this case the microstructure points to the occurrence of dynamical recrystallization during the deformation process. Moreover the presence of some Fe can be detected by X-ray microanalysis.

On the contrary the Fe areas show a cellular microstructure as one can expect from a plastically deformed sample, and no Cu can be detected within the microanalysis sensitivity.

The Fe concentration profile in the Cu matrix, measured with a nominal beam diameter of 20 nm, is reported in Figure 5 for two different deformation temperatures.

Considering that secondary fluorescence can be induced from the Cu photons into the pure Fe present on the other side of the interface, we have estimated this contribution with the following procedure.

Taking into account the fluorescence contribution the ratio between the apparent Cu and Fe concentrations can be written as:

$$\frac{C_{\text{Fe}}}{C_{\text{Cu}}} = K \frac{(I_{\text{Fe}} - F)}{I_{\text{Cu}}}$$

where C represent concentrations, I collected intensities of characteristic X-rays, F the secondary fluorescence contribution and K is the Cliff-Lorimer constant. The ratio F/I_{Cu} at a distance x

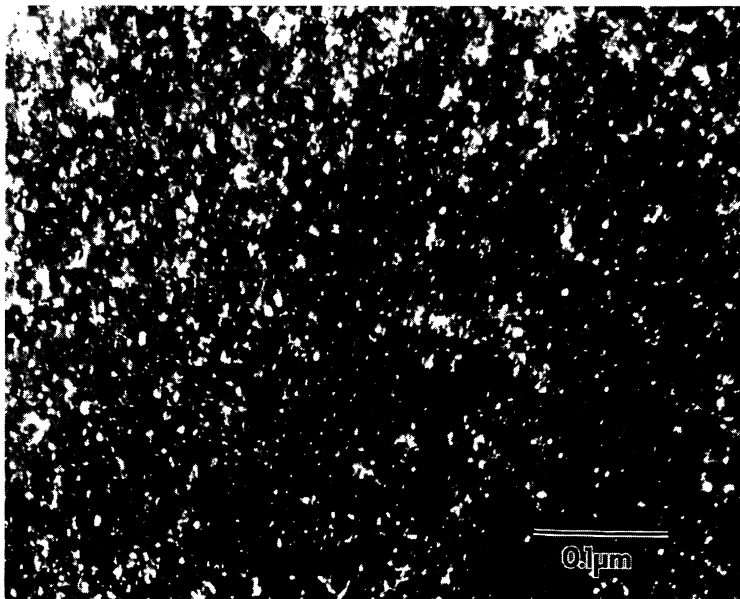


Fig. 4. — Weak beam image of a Cu grain in the trilayer sample deformed at 300 °C.

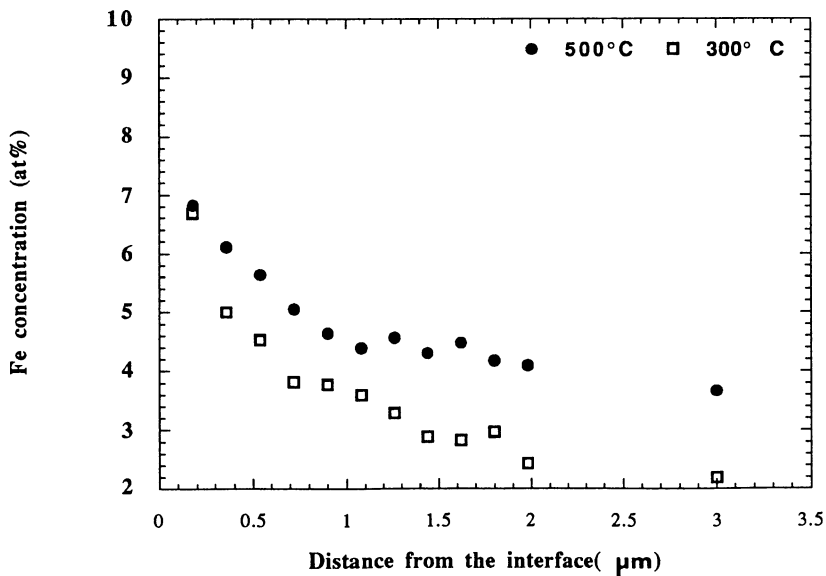


Fig. 5. — Experimental Fe concentration *versus* distance from the interface for trilayer samples deformed at different temperatures.

from the interface can be evaluated approximately with the following equation in the limit of small specimen thickness and with the additional hypothesis that all the Cu photons reaching the

interface are adsorbed by the Fe sheet:

$$F(x)/I_{\text{Cu}} = 2J\Omega \int_0^t \frac{x}{4\pi^2 (x^2 + y^2)^{3/2}} \exp - \left(\mu (x^2 + y^2)^{1/2} \right) dy$$

where t is the specimen thickness, y is a coordinate in the interface plane parallel to the specimen surface, μ is the absorption coefficient of Fe K radiation in Cu, J is the jump ratio at the Fe K absorption edge and Ω is the Fe K fluorescence yield.

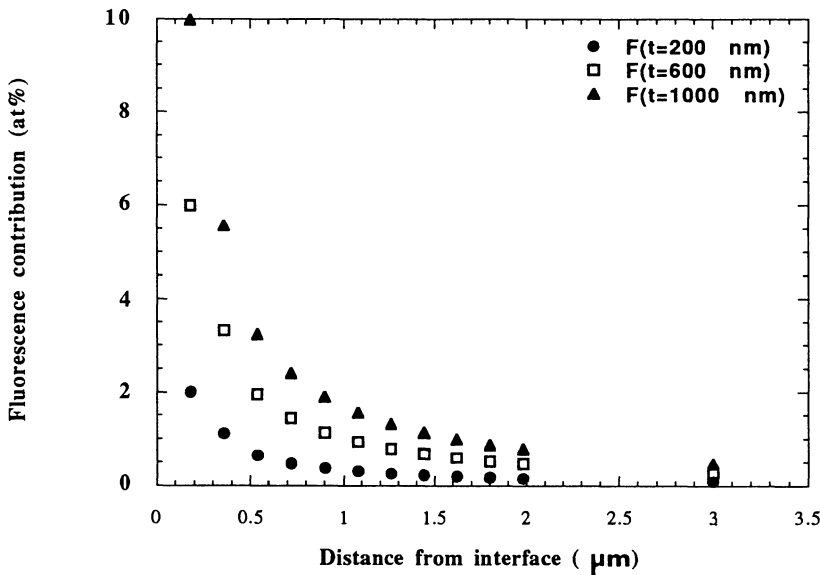


Fig. 6. — Fluorescence contribution computed for different specimen thickness.

This equation can be integrated analytically considering that for small values of y the exponential term can be expanded to first order, while for large values of the same parameter x can be neglected relative to y . The results of this computation are also reported in Figure 6 for different specimen thickness.

We want to remark that these approximations cause an over-estimate of the fluorescence contribution particularly in the region close to the interface, since we do not take into account that some photons entering into the solid angle defined by the interface itself can only travel a short distance into the Fe sheet with an absorption probability different from unity, since their trajectories are not normal to the Fe-Cu interface.

Even if a fully quantitative assessment is beyond the purpose of this work we can notice from Figures 5 and 6 how secondary fluorescence can contribute to the observed concentration increase close to the interface but it cannot account for the Fe concentration at larger distances. Moreover we notice that the experimental results are only slightly affected by the sample thickness showing again that the secondary fluorescence contribution, which, instead, is expected to grow linearly with the sample thickness is only a small fraction of the detected X-ray intensity. In conclusion we observe that some Fe diffuses into Cu during the deformation process increasing its local

concentration above the stable terminal solid solubilities at the processing temperatures. Moreover, even if the change in the boundary conditions of the diffusion process caused by the sample deformation prevents a quantitative determination of the effective diffusion coefficient from the concentration profile, we notice how the broad Fe profile points to apparent diffusivities higher by orders of magnitude with respect to the reported thermal tracer diffusion coefficient.

Discussion and Conclusions

All the experimental observations reported in this work seem to show that some alloying in the Fe-Cu system occurs even in the first stages of the high energy ball milling process. The alloyed grains have a size of several tens of nm and they appear to have a relatively low density of extended defects. Moreover several microstructural features seem to indicate that a high atomic mobility is operating during the milling process. In fact the presence of a low dislocation density, of oxide precipitates showing all the same orientation relationship with the matrix, probably due to a nucleation and growth process, indicate that some atomic rearrangement on a relatively long range occurs during or after the plastic deformation imparted to the powder by the ball collisions. Moreover the small intragranular voids could be caused by the condensation of an excess concentration of vacancies [11].

These findings are confirmed by the microstructure of the trilayer samples deformed in a more controlled way. The relatively large grain size with straight grain boundaries, the presence of many twins and the low density of dislocations show that also in this case atomic mobility is enhanced by plastic deformation at high strain rate. The large density of small defects can be due also for this kind of samples to the agglomeration of an excess concentration of point defects. We remark that these microstructural features are observed only on the Cu side of the interface, while the Fe crystals show a high density of dislocations arranged in a cellular structure, so that we deduce that only in the softer Cu dynamical recrystallization occurs.

The generation of point defects by the dislocation dynamics has been suggested several years ago [12, 13], so that it is not difficult to make the hypothesis that a high concentration of point defects is present in a material subjected to plastic deformation at a sufficiently high strain rate. This hypothesis is confirmed by the broad Fe concentration profile in the Cu matrix which is a direct measurement of atomic mobility during the process.

If we accept that a high excess concentration of point defects is induced by the plastic deformation in both kind of samples, we can suppose that also the thermodynamic equilibrium between the two metals is affected. In fact, considering that the chemical potential of Fe in Cu at the spinodal point is about 22 kJ/mole [9] and that the formation energy of a vacancy in Cu is about 1.25 eV, there is a driving force for a process of vacancy annihilation by a Fe jump across the interface. We can therefore conclude that the presence of Fe in the Cu matrix of the trilayer sample, where only one flat interface separates the two phases, is supporting this hypothesis, which in turn can also explain the microstructure of the ball milled samples.

References

- [1] Bormann R., *Materials by powder technology*, PTM 93, F. Aldinger Ed., DGM Informationsgesellschaft (Oberursel, 1993) p. 247.
- [2] Mazzone G., Montone A. and Vittori Antisari M., *Phys. Rev. Lett.* **65** (1990) 2019.

- [3] Martelli S., Mazzone G., Scaglione S. and Vittori Antisari M., *J. Less. Comm. Met.* **145** (1988) 261.
- [4] Cardellini F., Mazzone G. and Vittori Antisari M. *Acta Metall. Mater.*, in press.
- [5] Uenishi R., Kobayashi R., Naso S., Hatano H., Ishihara K.N. and Shingu P.H., *Z. Metallk.* **83** (1992) 132.
- [6] Ekert J., Holzer J.C., Krill III C.E. and Johnson W.L., *J. Appl. Phys.* **73** (1993) 2794.
- [7] Gente G., Ohering M. and Bormann R., *Phys. Rev. B* **48** (1993) 13244.
- [8] Yavari A.R. and Desré P.J., *Mater. Sci. Forum* **88-90** (1992) 43.
- [9] Yavari A.R., Desré P.J. and Benameur R., *Phys. Rev. Lett.* **68** (1992) 2235.
- [10] Martelli S., Mazzone G., Montone A. and Vittori Antisari M., *J. Phys. Colloq. France* **51** (1990) C4-241.
- [11] Arnaud B., Le Hazif R. and Martin G., *Acta Metall.* **33** (1985) 1105.
- [12] Nicholas J.F., *Acta Metall.* **7** (1959) 544.
- [13] Berghout C.W., *Acta Metall.* **6** (1958) 613.