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# ON THE EXISTENCE OF A NEW INTERMEDIATE NICKEL-BERYLLIUM PHASE

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## Introduction

Hardening of Iron-Nickel alloys, particularly the Invar type alloys, by Beryllium has been known for a long time [1]. We have however little information on the metallography of precipitation and the nature of Nickel-Beryllium precipitates in these alloys :

- There is a stable body centered cubic ordered phase NiBe, the parameter of which is a = 2.61 to 2.62 Å [2], known as $\beta$ phase.

- In a general review published in 1965, R.F. DECKER [3] suggests the existence of a $\gamma'$ $Ni_3Be$ phase. This suggestion was made [4] from the PEARSON and HUME-ROTHERY rule [5] that connects the $Ni_3$ X compounds stability to the size factor. Under this rule there should exist at least one metastable $Ni_3Be$ phase that transforms later to the equilibrium $\beta$ NiBe phase. The coherent non ordered face centered cubic metastable phase has been observed later by HORNBOGEN [6] in a Nickel - 7.27 % at.Beryllium alloy.

We have investigated, using transmission electron microscopy, precipitation at 700°C in an Iron - 40 % Ni alloy, hardened by Beryllium, the chemical analysis of which is shown in the next table :

Table I : Chemical Analysis (weight percent)

| Fe | Ni | Mo | Cr | Be |
|---|---|---|---|---|
| 50.5 | 40 | 5 | 4 | 0.5 |

Preparation of samples :

Samples are cylinders cut from bars supplied in the annealed condition. They are given a solution treatment during 30 minutes at 1100°C and then water quenched. Precipitation treatments are made in vacuo at 700°C during times running from a few seconds to 48 hours.
Thin foils cut from every sample are then examined inside an electron microscope.

Precipitation at 700°C :

In the solution treated condition electron diffraction patterns show no evidence of precipitation : the alloy appears mainly as a face centered cubic solid solution of parameter $a_\gamma = 3.57$ Å. However it still contains primary constituents which were not put into solution ; they have a size of a few microns and have been identified from electron diffraction patterns to the $\beta$ NiBe phase.

After aging at 700°C is observed continuous precipitation of a phase that appears in the shape of discs or plates located in the $\{100\}$ matrix planes. Figure I A micrograph shows $\beta'$ precipitation after aging one hour at 700°C. It concerns a (100) foil area on which precipitates located in the two $\{100\}$ planes perpendicular to the foil surface can be seen owing to the distortion they introduce in the surrounding matrix. Precipitates lying on planes parallel to the foil surface can hardly be observed. Figure I B electron diffraction pattern shows all extra spots due to $\beta'$ precipitation. Streaks related to the plate or disc shape of precipitates also appear in the $\langle 100 \rangle$ directions. Only precipitates lying on one $\{100\}$ plane are seen on figure I C dark field micrograph obtained by selecting the spot which has been encircled on figure I B.

From all diffraction patterns the structure of $\beta'$ can be determined : it is a body centered tetragonal phase with parameters [7] :

$$a_{\beta'} \sim 2.53 \text{ Å}$$
$$c_{\beta'} \sim 2.64 \text{ Å}$$

accuracy on these values being about $\pm .01$ Å

$\beta'$ orientation relationship in the $\gamma$ matrix is :

$$\begin{cases} [100]_{\beta'} \parallel [011]_{\gamma} \\ [001]_{\beta'} \parallel [100]_{\gamma} \end{cases}$$

$[001]_{\beta'}$ can be parallel to anyone of the $\langle 100 \rangle_{\gamma}$ directions. The $a_{\beta'}$ parameter being equal to half the length of the matrix cube face diagonal, $\beta'$ is coherent in its basal plane and non coherent in the $\vec{c}_{\beta'}$ direction : it is a semi coherent phase. All precipitate spots appear on electron diffraction patterns so $\beta'$ is likely to be ordered.

In order to avoid any possible mistake between $\beta'$ and a fully coherent phase, the presence of $\beta'$ has been systematically investigated on dark field micrographs obtained by selecting with the objective diaphragm the $(001)_{\beta'}$ spot which cannot be taken in place of any spot coming from a coherent phase. $\beta'$ phase is present after the shortest aging time we were able to perform that is a few seconds. Few alignment effects have been observed and it seems that $\beta'$ is obtained by homogeneous nucleation.

If for short aging times $\beta'$ precipitates shape is close to discs shape, it changes, for long aging times : figure II micrograph is a dark field micrograph showing precipitates shape after aging 48 hours at 700°C : they are plates the contours of which are not geometrically simple. We think that the contrast which is observed at the surface of $\beta'$ precipitates is due to the presence of ledges [8] which can be interpreted as growth or dissolution steps. Such a ledge can be seen on A precipitate on figure II. In the same way in the area marked B a precipitate dissolves while its neighbour C grows. Ledges appear on C precipitate.

$\beta'$ can be put again into solution by discontinuous precipitation of the ordered body centered cubic stable $\beta$ NiBe phase (figure III). The alloy chemical composition, the existence of denuded zones around $\beta$ NiBe precipitates on grain boundaries together with the observations we have made on $\beta'$ suggest that it is a Nickel-Beryllium phase that can obviously dissolve other elements.

The body centered tetragonal $\beta'$ phase can be considered either as a deformed face centered cubic phase or a deformed body centered cubic phase : it has the crystallographic characteristics of an intermediate phase between the metastable coherent face centered cubic $Ni_3Be$ phase the existence of which was suggested by DECKER and the stable non coherent body centered cubic $\beta$ phase. We have observed the $\beta' \rightarrow \beta$ transformation by discontinuous precipitation. We have not observed the $Ni_3Be \rightarrow \beta'$ transformation. It could be due to the fact that the aging temperature was too high.

Conolusions :

- We have shown the existence, in an Iron - 40 % Nickel alloy hardened by Beryllium, after aging at 700°C, of a new Nickel-Beryllium phase, we call $\beta'$, which has a body centered tetragonal struoture.

-$\beta'$ parameters and orientation relationship in the matrix have been determined : $\beta'$ is a semi coherent phase.

-$\beta'$ shows the crystallographic characteristics of an intermediate phase between the metastable $Ni_3Be$ phase and the stable $\beta$ NiBe phase.

Acknowledgement

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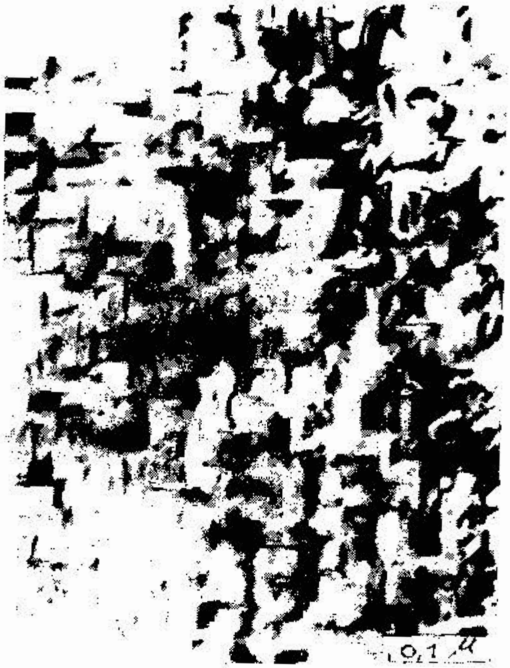
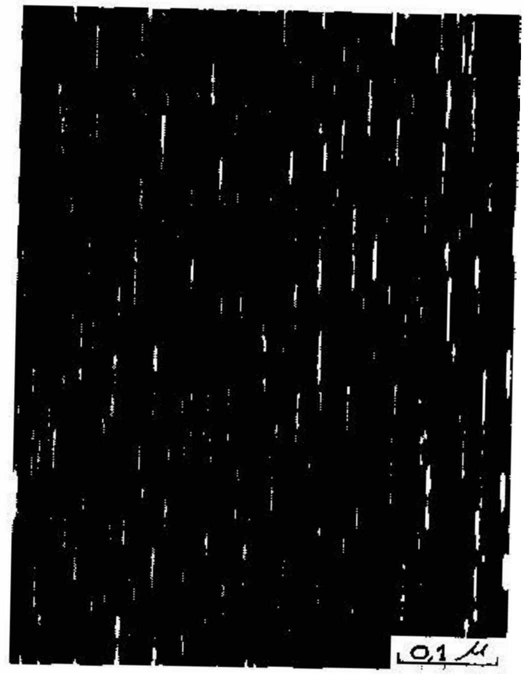
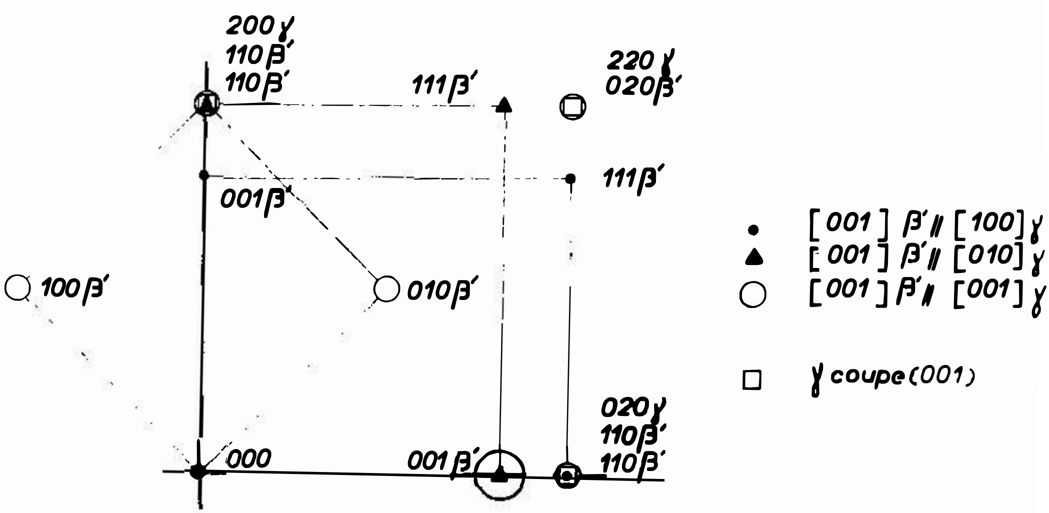



I A




I C




I B

FIG. I : β' PRECIPITATION AFTER AGING 1 HOUR AT 700°C

A - Transmission micrograph of a (100) foil area.


FIG. II : β' PRECIPITATION AFTER AGING 48 HOURS AT 700°C
(100) foil-dark field micrograph using $(100)_{\beta'}$ reflection.


FIG. III : DISCONTINUOUS PRECIPITATION OF β NiBe.

DISCUSSION

A. Guinier — The phenomenon in this alloy seems very similar to the aging of CuBe or NiBe. Did you observe striations on the surface of the specimen during precipitation ? Have you some information about the possible existence of zones before the precipitation ?

J.C. Mazaud — We did not observe striations on the surface of the specimens during precipitation. But we did not indeed pay any particular attention to this phenomenon. We have studied precipitation between 650 and 730°C. After the shortest aging times we were able to carry out we always observed $\gamma'$ precipitation. We think that there could exist zones before precipitation at the beginning of beryllium atoms (clustering).