Investigation of a silicon nitride/ferrite gradient composite for lightweight structure applications

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One common design criterion for structural material is achieving minimum mass while withstanding a certain load. This ongoing race toward ever stronger and lighter materials has been sparked off and fueled by various fields of industry, be it aerospace, aeronautics, automotive, sports equipment or civil engineering. It is now generally accepted that monolithic materials will only take us so far. In consequence, materials suppliers worldwide are now focusing much attention and effort on composite materials. Indeed, composites are the key to attain the combination of otherwise incompatible properties, for instance hardness and ductility. However, complex and costly manufacturing processes are usually involved in order to obtain homogeneous composites with strong interfaces between their components. The work presented here explores an innovative concept of silicon nitride/ferrite composite conveniently obtained by nitriding a sheet of Fe-Si alloy. Intragranular precipitation of silicon nitride in the matrix occurs in the form of nanosized particles. Synthesizing the reinforcement ceramic in this particular fashion also gives rise to a precipitation gradient in the material related to the nitrogen diffusion kinetics. The resulting sheet is strong and lightweight versus standard steel sheets while remaining comparably cost-effective. The results exhibited below show that the nanoprecipitates of silicon nitride feature the odd combination of a cubic morphology and amorphous structure. The stability of these precipitates is also of interest and it is shown below that they crystallize upon annealing.

Specimens utilized in this study were prepared from cold rolled Fe-1.5 wt.% Si and Fe-3.3 wt.% Si alloys. They were annealed so as to obtain an equiaxed ferritic microstructure with an average grain size of roughly 35 µm. They were subsequently nitrided through either gaseous or plasma routes at 570°C for determined durations. A part of these specimens was further annealed at 570 °C for 20 h. Thin foils were sampled from these specimens grinding them down to 60 µm before electrolytic thinning with a Struers Tenupol 5 in a 95 vol.% 2-butoxyethanol/5 vol.% perchloric acid electrolytic bath at 27 V. Several foils were also prepared via focused ion beam (FIB) milling. Observations of the foils were carried out using two transmission electron microscopes (TEM), a Philips CM200 as well as a Jeol 2010-F both operated at 200 kV.

Bright field TEM images of thin foils right after nitriding showed precipitates with sizes ranging from 15 nm to 75 nm displaying a cubic morphology with a rather poor contrast with the matrix. No electron diffraction pattern specific to these precipitates could be obtained, supporting their amorphous nature which had been previously reported [1]. High resolution TEM images unequivocally confirm it as shown in figure 1. The stoichiometry of these precipitates has been assessed by energy dispersive X-ray spectroscopy (EDXS) and parallel electron energy loss spectroscopy (PEELS) and both techniques yielded a formula close to Si_3N_4. Extractive replicas and high angle annular dark field (HAADF) STEM images allowed a better appraisal of the actual volume fraction of silicon nitride in the sample, which can reach up to several tens of percent depending on the sample and the depth in the sheet as it can observed in figure 1.

After annealing, bright field TEM images revealed elongated particles showing a hexagonal base with a diameter nearing 70 nm. EDXS and PEELS analyses once more suggest their formula is very close to Si_3N_4. An electron diffraction pattern associated with these particles could be identified and

it was found that these precipitates are α-Si_3N_4 as shown in figure 2. It was subsequently possible to determine the Orientation Relationship (OR) between this phase and the ferritic matrix and it was discovered to be $(110)_{\alpha\text{-Fe}}//(100)_{\alpha\text{-Si3N4}}$ with $[111]_{\alpha\text{-Fe}}//[001]_{\alpha\text{-Si3N4}}$. It is planned to confront this observation to OR prediction models such as the coincidence of reciprocal lattice points (CRLP) model [2].

In conclusion, it has been successfully shown, using a set of TEM techniques that amorphous Si_3N_4 precipitates intensely in the form of nanosized cube-shaped particles upon nitriding of ferritic Fe-Si alloys. The high precipitate volume fraction is such that it leads to a notable decrease of the composite density and an important increase of its hardness. Besides, it has also been demonstrated that these precipitates crystallize upon annealing in α-Si_3N_4 in the form of hexagonal base prism and the OR of this phase with respect to the matrix could be determined.

References

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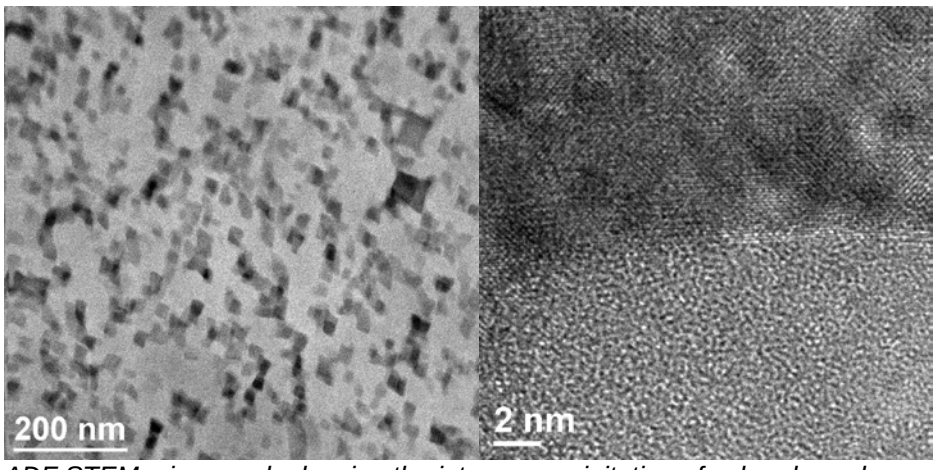

Figure 1. *a) HAADF STEM micrograph showing the intense precipitation of cube-shaped amorphous Si_3N_4 particles in samples as nitrided. b) HRTEM micrograph confirming the amorphous structure of the Si_3N_4 precipitates.*

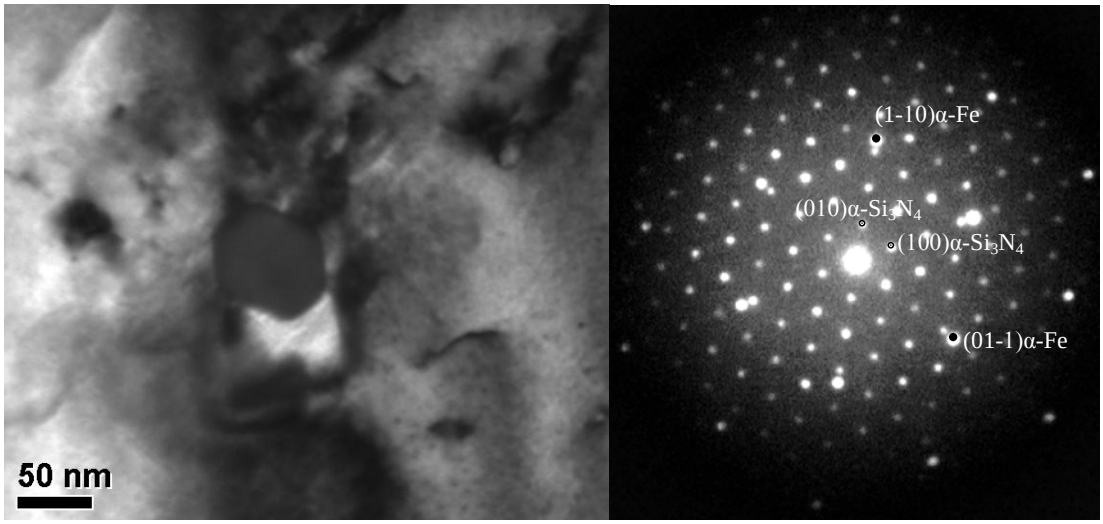

Figure 2. *Bright field TEM micrograph showing the hexagonal base of α-Si_3N_4 prism originating from the amorphous/crystalline transition of the precipitates in the ferrite matrix. The electron diffraction pattern in insert shows the OR* $(10\text{-}1)_{\alpha\text{-Fe}}//(100)_{\alpha\text{-Si3N4}}$ with $[111]_{\alpha\text{-Fe}}//[001]_{\alpha\text{-Si3N4}}$.