



Competitive precipitation of amorphous and crystalline silicon nitride in ferrite: Interaction between structure, morphology, and stress relaxation

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Abstract—We present a detailed analysis based on both experimental and modeling approaches of the unique silicon nitride precipitation sequence recently observed in ferritic Fe–Si alloys upon nitriding. At 570 °C, silicon nitride forms as an amorphous phase of size-dependent cuboidal morphology which results from the symmetry of matrix crystal structure. These amorphous precipitates are stable over remarkably long treatment durations. However, we demonstrate here that it is possible to trigger a transition to the precipitation of a crystalline modification of Si₃N₄ by switching to a denitriding medium at the same temperature. This change in structure is associated with a change from the cube-like morphology to a hexagonal prism shape. This unique phenomenon, driven by a classical nucleation and growth process, can be explained by the shift of stress-relief mechanism related to the change of atmosphere. The plentiful availability of nitrogen atoms during nitriding allows a strong relaxation of the precipitation-induced stress, which is energetically more favorable to the amorphous phase. Upon annealing in a low nitrogen activity medium, nitrogen in solid solution diffuses outward and no longer relieves the precipitation-induced stress. In that configuration, the crystalline modification of Si₃N₄ becomes more stable owing to its lower associated stress. It precipitates in a hexagonal prism shape, which is the equilibrium shape dictated by the crystal symmetries of both the matrix and the precipitates.

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1. Introduction

Precipitation reactions in solid-state materials can lead to dramatic variations of their physical properties. Precipitation treatments have thus become a popular tool to tailor the properties of both structural and functional materials. To do so, it is invariably essential to be able to control the state of precipitation in the material in terms of precipitate phases, their morphology, mean size and number per unit volume. Typical treatments involve a solutionizing step followed by one or more isothermal precipitation steps during which the desired population of precipitates is allowed to form.

The precipitation of silicon nitride in ferrite is one example of such treatments. This precipitation can notably be exploited to strengthen and lighten sheets of silicon-rich steel [1]. In order to obtain an adequate volume fraction of nitride precipitates, the required nitrogen cannot be introduced during liquid state processing of the alloy due to the limited solubility of nitrogen in liquid iron. Thus, nitrogen is introduced in solid state by nitriding the alloy at 570 °C. The precipitation of silicon nitride takes place simultaneously at this temperature. This method has many advantages. It notably makes solutionizing treatments superfluous. It also allows for very large amount of nitrogen to be introduced at a relatively low temperature. This leads to considerable solid solution super saturation while substitutional atoms have limited diffusion capabilities resulting in a very fine but very abundant precipitation, which is an optimal configuration for precipitation hardening. Unlike any other nitride, silicon nitride precipitates in ferrite either as an amorphous or crystalline phase. An

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adjustable mix of the two phases can be obtained with adequate processing parameters.

The literature dealing with the Fe–Si–N ternary systems that pre-dates the 21st century is scarce and elliptical at best, even contradictory sometimes. In a study dated from 1955, silicon was suspected to form a mixed nitride with iron at 700 °C that could not have been identified [2]. Later work on nitriding between 500 and 800 °C concluded that this assumption was wrong and that silicon nitride precipitated in two crystalline phases of identical stoichiometry [3]. These phases were identified as α -Si₃N₄ and β -Si₃N₄, both well known in bulk silicon nitride, although α is said to have a fraction of its nitrogen substituted with oxygen depending on experimental conditions. In much more recent research, it has been shown that during nitriding at 570–580 °C, silicon nitride precipitates abundantly in Fe–Si binary alloys in fine stoichiometric Si₃N₄ precipitates [1,4–6]. These nanoprecipitates display the odd combination of an amorphous structure with a cuboidal morphology. The amorphous structure was found to be stable in a nitriding atmosphere for as long as 825 h (over a month) [5]. At 650 °C, they switch to an octapod shape after longer nitriding time while retaining their amorphous structure but a population of crystalline α -Si₃N₄ precipitates simultaneously [7]. Upon annealing at 580 °C in a non-nitriding or denitriding atmosphere, we have recently demonstrated that a crystalline phase nucleates and grows in the nitrided alloys at the expense of the preexisting amorphous phase [6]. This crystalline phase precipitates in the form of hexagonal prisms and conserves the stoichiometric Si₃N₄ composition. In addition, diffraction patterns indicate the presence of a threefold symmetry axis.

The sole fact that Si₃N₄ precipitates as an amorphous phase (α -Si₃N₄) in a crystalline (α -Fe) matrix is already quite remarkable given the short list of other examples available in the literature [8–11]. It is also a counter intuitive event as crystalline phases are in a vast majority of cases energetically more favorable. In the few anterior examples mentioned, no explanation has been given as to why the amorphous phase occurred instead of the crystal. In the present case, it has been suggested that the amorphous silicon nitride remains stable in a wide range of conditions due to exceedingly slow crystallization kinetics [5]. The fact that it develops a cubic shape consistently oriented with the matrix is also quite intriguing. It suggests that the matrix alone imposes its shape to the growing precipitate, an uncommon scenario in ferrous alloys. The main originality of the system however is the transition it operates from the precipitation of an amorphous phase to the precipitation of a crystalline one as a function of the medium in which it is annealed. This unique feature represents a chance to gain valuable insights on both the thermodynamics and the kinetics involved in the precipitation cycle and the possibilities it opens up.

In the first part of this paper, the characterization of the initial amorphous precipitation is followed by a detailed explanation of the mechanism that leads to the evolution of the morphology and the stabilization of the structure.

In the second part, experimental evidence of the transition from amorphous to crystalline precipitates is presented along with a discussion of the factors triggering this transition, linking structure, stress relaxation and morphology.

2. Experimental details

2.1. Alloy chemistry and processing

2.1.1. Casting and rolling

All the experimental results presented in this work were acquired on samples obtained from thin sheets of two binary Fe–Si alloys noted “Fe–1.5 Si” and “Fe–3.3 Si”. Their compositions are reported in Table 1. These alloys were first cast in 60 × 125 × 240 mm³ ingots. They were then hot rolled down to a 3 mm thickness. The hot-rolling end temperature was 850 °C. The resulting sheets were cooled at a rate of 30 °C s⁻¹ down to 580 °C and at 20 °C s⁻¹ afterward down to room temperature. They were next cold rolled by roughly 70% to a thickness nearing 1 mm. They were eventually annealed at 750 °C during half an hour to recrystallize ferrite.

2.1.2. Nitriding and denitriding

Prior to nitriding, samples of 75 × 10 × 1 mm³ were cut from the annealed sheet. They were ground down to P2400 grit before being cleaned in an ultrasonic cleaner in ethanol. These samples subsequently underwent Plasma Assisted Nitriding (PAN). This treatment begins with a heating stage in a 50% H₂/50% Ar mix at a 3 mbar pressure in a 200 sccm total gas flow during which the heat is supplied by the pulsed DC plasma. This step also serves the purpose of further cleaning the surface of the sample. When the 570 °C treatment temperature is reached, the gas mix is switched to 50% H₂/50% N₂ and nitriding actually begins. After the treatment duration, the plasma is interrupted and the sample is left to cool down to room temperature at a reduced pressure (10⁻² mbar).

In order to determine the effect of atmosphere on the stability of nitrides, it was decided to anneal the nitride samples at the same temperature but in an atmosphere that would remove practically all the available nitrogen from the ferritic solid solution. This was achieved by annealing in 100% N₂ at 1 atm.

2.2. Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) thin foils were prepared from sheet samples ground to a thickness approaching 80 μ m comprised between depths ranging from about 70 to about 150 μ m from the nitrided surface. Disks of 3 mm in diameter were then punched from the foil thus obtained. These disks were electrochemically thinned in a Struers Tenupol 5 in a 95 vol.% 2-butoxyethanol/5 vol.% perchloric acid electrolytic bath at 27 V around 10 °C. The resulting thin foils were thoroughly rinsed in ethanol, before being cleaned in a Gatan Solarus 950

Table 1. Chemical compositions of the as-cast binary Fe–Si alloys (10⁻³ wt.%).

	C	Mn	S	P	Si	Cr	Mo	Ni	Ti	Cu	B (ppm)	N
Fe–1.5 Si	3	10	1	2	1490	21	2	<2	59	2	<3	<2
Fe–3.3 Si	3	10	1	2	3360	21	2	<2	60	2	<3	<2

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