THE OCCURRENCE OF HIGH-SPEED STEEL CARBIDE-TYPE η PHASES IN THE Fe–Nb SYSTEM

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Summary

The high-speed steel carbide-type η phase claimed to exist in the Fe-Nb system at a composition Fe₂Nb₃ is an interstitial oxide, η -Fe₆Nb₆O. It is obtained by heating Fe-Nb alloy powders in sealed and evacuated vitreous silica capsules at 1000 °C. A second η phase with larger unit-cell dimensions is obtained by hydrogen treatment of Fe-Nb alloys at 1000 · 1200 °C; it is an interstitial nitride, η -Fe₃Nb₃N, formed because even "purified" hydrogen contains small concentrations of nitrogen. Examples of oxide formation by heat treatment of metals in vitreous silica and of nitride formation by heat treatment in hydrogen are not uncommon.

1. Introduction

As well as the Laves phases ϵ -Fe₂Nb previously reported (see ref. 1), Goldschmidt [2, 3] claimed three additional intermediate phases in the Fe– Nb system. These were σ -Fe₂₁Nb₁₉ isostructural with σ -FeCr, η -Fe₂Nb₃ with a high-speed steel Fe₃W₃C-type structure, and a niobium-rich phase of inexact composition Fe_xNb_y and unknown structure. Kripyakevich *et al.* [4] reported a rhombohedral μ phase at about FeNb and from a crystal structure determination showed that its composition should be written as (Fe_{6.5}Nb_{0.5})-Nb₆ to correspond with the μ -phase prototype Fe₇W₆. Although Raman [5, 6] concluded that ϵ and μ were the only intermediates in the system, the phase diagram proposed on the basis of Goldschmidt's work and shown in Fig. 1 has been generally accepted [7, 8].

During the nitriding of Fe–Nb alloys, the present authors found that heat treatment at 1200 °C in flowing hydrogen of an Fe–1.0wt.%Nb alloy containing ϵ precipitates converted the latter to an η -type phase. It was considered unlikely that η structures exist without the presence of interstitial atoms, and so trace impurities of carbon, nitrogen or oxygen in the hydrogen

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Fig. 1. The Fe-Nb phase diagram. (After Elliott [7].)

were suspected. A re-investigation of the Fe–Nb system was therefore made in an attempt to explain Goldschmidt's observation of the occurrence of the η phase.

2. Experimental details

Buttons, 5 g in mass, of eleven alloys with compositions from $\text{FeNb}_{0.5}$ to FeNb₉ were made by melting together the pure metals under argon in a small arc furnace using a non-consumable tungsten electrode and a water-cooled copper hearth. The products were powdered in a steel mortar or filed, depending on their brittleness. They were then characterized by X-ray methods in the as-cast condition and after annealing at 1000 - 1200 °C for periods of up to twenty-one days in evacuated and sealed vitreous silica capsules. The powdered alloys were also examined after carburizing, nitriding and oxidizing.

3. Results

3.1. Phase characterization in the Fe-Nb system

At the composition Fe₂Nb a single, homogeneous Laves phase ϵ was observed under all conditions. At FeNb the X-ray diffraction pattern was entirely different from that of the σ phase reported by Goldschmidt but was identical with the rhombohedral μ phase and had the same equivalent hexagonal cell dimensions (a, 4.929 Å; c, 26.80 Å; c/a, 5.44) as given by Kripyakevich *et al.* [4]. The range of homogeneity of μ is small and all nine alloys richer in niobium than FeNb, *i.e.* with compositions from FeNb_{1.5} to FeNb₉, gave μ plus the Nb(Fe) terminal solid solution under all conditions.



Fig. 2. The Fe-Nb phase diagram. (After Raman [6].)

Contrary to the findings of Goldschmidt, there was no evidence in any as-cast or annealed alloy of σ or η phases or of his unidentified Fe_xNb_y phase. The present observations are entirely consistent with the Fe-Nb phase diagram proposed by Raman [6] and shown in Fig. 2.

3.2. The occurrence of η phases

Since no binary intermetallic η phase was observed it seemed that Goldschmidt's phase must have been an interstitial alloy. Attempts were therefore made deliberately to introduce interstitial atoms into the binary Fe-Nb alloys already prepared.

3.3. Preparation of η nitride

By nitriding the alloy powders in NH₃:H₂ and N₂:H₂ gas mixtures three different Fe-Nb nitrides were obtained with an η phase occurring at the lowest nitrogen potential. However, even when FeNb and FeNb, were nitrided with a low nitrogen partial pressure, e.g. in 5N₂:95H₂ at 850 °C, the η phase was not obtained pure. In initial experiments (see Introduction) η had been observed after heat treatment of Fe-1.0wt.%Nb in hydrogen at 1200 °C; also at Newcastle, Nutter [9] had obtained a ternary nitride by hydrogen reduction of nickel and molybdenum mixed oxides at high temperatures where the small nitrogen impurity in the hydrogen provided the necessary nitrogen potential. The same methods were therefore pursued and pure η phase was obtained by hydrogen treatment of the alloy FeNb at 1000 - 1200 °C. All reflexions in the X-ray diffraction pattern of the product were indexed on a cubic unit cell with $a = 11.347 \pm 0.001$ Å; chemical analysis gave the composition Fe₃Nb₃N within experimental error. Similar treatment of alloys with less niobium (e.g. FeNb_{0.5}) gave $\eta + \alpha$ -Fe but with higher niobium content (e.g. FeNb₂) an unidentified phase occurred with η . The variation of the unit cell dimensions of the η phase was negligible showing that there was no detectable range of homogeneity.

3.4. Preparation of η oxide

 η oxides were obtained by heating Fe–Nb alloy powders with small amounts of FeO in an evacuated and sealed silica tube for 48 h at 1000 °C. With FeNb_{1.5} the product was η phase plus niobium. The same η phase with similar cell dimensions ($a = 11.251 \pm 0.005$ Å) was obtained with niobium by heating FeNb₃ powder at 1000 °C in a sealed silica tube. The FeNb₃ powder had been exposed to the atmosphere for several months and had an analysed oxygen content of 0.3 wt.%. After heat treatment, analysis gave 0.6 wt.% oxygen. For the reaction

$$6FeNb_3 \xrightarrow{O} Fe_6Nb_6O + 12Nb \tag{1}$$

the oxygen content of the product should be 0.79 wt.%.

Finally, iron and niobium powders in the ratio 2Fe:3Nb with oxidized surfaces were arc melted and gave η -phase oxide plus niobium with 1.5 wt.% O in the product. The reaction

$$3Fe_2Nb_3 \xrightarrow{O} Fe_6Nb_6O + 3Nb$$
 (2)

requires 1.35 wt.% O and so the products of both reactions (1) and (2) suggest that the η phase is an η oxide of composition Fe₆Nb₆O. Prolonged hydrogen reduction of the product of reaction (2) gave μ phase + Nb,

$$\begin{array}{c} \operatorname{Fe}_6 \operatorname{Nb}_6 \operatorname{O} + \operatorname{H}_2 \longrightarrow \operatorname{6FeNb} + \operatorname{H}_2 \operatorname{O} \\ \eta \text{ phase} & \mu \text{ phase} \end{array} \tag{3}$$

as might be expected if the proposed composition of η is correct.

The observed unit-cell dimension of the η oxide $(11.251 \pm 0.005 \text{ Å})$ is considerably smaller than that of Fe₃Nb₃N $(11.347 \pm 0.001 \text{ Å})$ and the difference is greater than would be expected from comparison between Fe₃Mo₃O $(11.077 \pm 0.001 \text{ Å})$ and Fe₃Mo₃N $(11.082 \pm 0.001 \text{ Å})$; this suggests a smaller interstitial atom concentration than M₆X for the Fe–Nb oxide and so supports the proposed Fe₆Nb₆O.

3.5. η carbides

All attempts to prepare η carbides by arc melting and heat treatment of mixtures of Fe-Nb alloy powders with carbon were unsuccessful. In all cases only the very stable niobium carbides were formed.

4. Discussion

The present work shows that ϵ and μ are the only intermediate phases in the binary Fe-Nb system, and that η exists only as an interstitial alloy nitride or oxide. It is common in metallurgical technology to equilibrate alloy samples by heating in evacuated and sealed silica capsules for prolonged periods at high temperatures. It is often not appreciated that the oxidizing potential of a vitreous silica container or reaction tube, evacuated or containing pure hydrogen, is not negligible. Types II and III vitreous silica manufactured respectively by flame fusion of quartz crystal and by hydrolysis of silicon tetrachloride [10] contain \equiv Si-OH groups in the glass structures which establish a significant partial pressure of water vapour at temperatures above 500 °C. Even with type I vitreous silica manufactured by electric fusion of quartz crystal powder, hydrogen reacts with it to produce a water vapour pressure [11]. These facts explain why aging a pure iron wire in an evacuated type II silica tube at 500 °C produces a surface layer of FeO; and why pure hydrogen passed over an alloy of Fe-5wt.%Mo at 800 °C gives η -Fe₃Mo₃O in a silica reaction tube but not in a pure alumina tube. It seems certain that Goldschmidt's incorrect characterization of Fe₂Nb₃ as an η -phase high-speed steel carbide-type structure was due to oxidation by vitreous silica.

The formation of nitrides by heat treatment of alloys in hydrogen is also not impossible because purified electrolytic hydrogen contains about 0.05 vol.% N₂ and, as shown elsewhere [9, 12], an Ni-Mo alloy will react with nitrogen, even in gas mixtures with high H₂:N₂ ratios, at temperatures below 1300 °C to form ternary Ni₂Mo₃N. In the same way, FeNb alloy gives η -Fe₃Nb₃N.

There must be many other examples in the literature where incorrect compositions or structures have been assigned to alloy phases. It seems doubtful whether any of the claimed η structures containing no interstitial atoms, *e.g.* Ti₂Cu and Ti₂Ni, can really exist.

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