Nanoindentation Study on Solid Solution Softening of Fe-rich Fe₂Nb Laves Phase by Ni in Fe-Nb-Ni Ternary Alloys

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Abstract

In an attempt to understand the solid solution softening by Ni of an Fe-rich Fe₂Nb Laves phase that is in equilibrium with γ -Fe, we have examined the defect structure in the Laves phase in Fe-Nb-Ni alloys by transmission electron microscopy, and its hardness as a function of orientation and solute (Ni) content by nanoindentation. The binary Fe-rich Laves phase and the ternary Laves phases with lower Ni content (18 %) exhibit a featureless morphology with low dislocation density, whereas the ternary Laves phase with higher Ni content (33 %) includes basal planar faults extending to several micrometers, producing a local change in the stacking sequence of the three 3⁶-nets (triple layer) of the C14 structure. The hardness of the binary and the ternary Laves phases with 18% Ni in solution is almost constant and independent of orientation, whereas the ternary Laves phase with 33 % Ni in solution exhibits a substantial dependence of hardness on orientation and this dependence appears associated with the ease of basal slips evidenced by slip traces around nanoindents. The relative ease in activating basal slip in the presence of a large amount of Ni in solution is thought to be the dominant contributor to the observed solid solution softening.

1. Introduction

A common class of intermetallic compounds with the AB_2 stoichiometry and complex crystal structures is Laves phase. This phase occurs as binary compounds, typically over a small range of compositions, with sometimes extensive solubility for a third element, and occasionally, as uniquely ternary compounds in some systems. In some instances however, such as in the binary Fe-Nb system that is the subject of this study, the C14 Fe_2Nb Laves phase can be stable at compositions that are significantly off-stoichiometric. The more common forms are the hexagonal C14 and cubic C15, with a minor form of the hexagonal C36 type [1]. These phases are notoriously brittle at ambient temperature, their brittleness being attributed to the difficulty in moving dislocations under an applied shear stress [1-4]. These compounds are often present in many multiphase alloys, and are believed to have a detrimental effect on the overall mechanical properties, particularly, ductility and fracture toughness at ambient temperatures [5].

As a part of our on-going effort to develop novel austenitic heat-resistant steels strengthened by thermodynamically stable Laves phase, the phase equilibrium between γ -Fe and Fe_2M Laves phases (C14 structure) has been systematically examined in Fe-M-Ni ternary systems (M: Nb, Ti, Mo) at elevated temperatures [6-10]. Takeyama and coworkers have recently proposed a new austenitic heat-resistant steel, a carbon-free alloy with the composition Fe-20Cr-30Ni-2Nb (at%) that is strengthened by thermodynamically stable TCP (topologically close-packed) Laves phases and other GCP (geometrically close-packed) phases [7,8,11]. They demonstrated that this steel exhibits superior long-term creep rupture strength due to the Laves phase sufficiently covering grain boundaries [11-13]. Extensive phase diagram studies demonstrated that in the Fe-Nb-Ni

ternary system, a homogeneity region of the Fe₂Nb Laves phase with the C14 structure extends towards the equi-Nb concentration direction up to 44 at.% Ni [10]. This indicates that more than two thirds of the Fe sublattice sites in Fe₂Nb can be replaced by Ni atoms. The solute Ni atoms preferentially replace Fe₂ sublattice site in C14 structure, as revealed by XRD measurement [14]. An interesting finding in the Fe-Nb-Ni ternary Laves phase is the significant solid solution softening measured in the Fe-rich Laves phase (in equilibrium with γ -Fe). The hardness of Laves phase measured by Vickers indentation is plotted as a function of solute Ni content in Fig.1. A part of the hardness data and the chemical compositions have been shown elsewhere [6,10]. We note that the hardness of the Fe-rich Laves phase decreases substantially with increasing Ni content, especially beyond 25 at. % Ni and up to about 40 at.% Ni from 9.1 GPa to 4.5 GPa. Whether a similar response is present for the stoichiometric Laves phase is not known as compositions with Ni (substitution for Fe) greater than 20% were not examined. Associated with these measurements is a large scatter in Vickers hardness values. The origin of this scatter is not clear but could be associated with the change in hardness of the Laves phase with orientation (i.e. basal slip). Ni in solid solution may enhance the plastic deformability of the Laves phase by facilitating synchroshear and promoting basal slip [15-17], resulting in solid solution softening. We have recently demonstrated the possibility of plastic deformation by slip in compression at room temperature in single crystal micropillars of a Fe-Nb-Ni ternary Laves phase [18]. Another possible reason for the scatter in the Vickers hardness may be related to the presence of the soft surrounding γ -Fe phase. Thus, the observed hardness change is attributable to different intrinsic and extrinsic factors, making it difficult to isolate solid solution softening as the

dominant effect. To further elucidate this effect, in the present study, we have examined the hardness of Fe-rich Fe₂Nb Laves phases (in equilibrium with γ -Fe) by nanoindentation as a function of orientation and Ni content in solid solution in the Laves phase. The observations are then utilized in conjunction with previous results to understand the origin of solid solution softening.

2. Experimental procedure

The alloys examined in this investigation are nominally Fe-15Nb-X alloys where X represents Ni ranging from 0 to 40 at.% (Fe-15Nb-(0, 20, 40)Ni), and hereafter all compositions are given in atomic percent (at. %) unless otherwise noted. These alloys were prepared by arc-melting and each weighed about 30 g. The prepared alloys were cut into pieces and then equilibrated at 1473 K for 240 hours, followed by a water quench to room temperature. **Figure 2** shows the isothermal section of the Fe-Nb-Ni ternary phase diagram at 1473 K [10]. Compositions of these alloys fall within the two phase region of γ -Fe and Fe₂Nb Laves phase. The specimens for optical microscopy and scanning electron microscopy (SEM) were mechanically polished, followed by electropolishing in a Cr-saturated phosphoric acid solution at 35V, 0.5A for 30s at 337 K. The phases and crystallographic grain orientation were analyzed by EBSD (TSL solutions, OIM Data Collection and OIM analysis). Thin discs for transmission electron microscopy (TEM) were cut from the heat treated alloy, mechanically polished, and twin-jet electro-polished in a solution of ethanol with 12 vol.% perchloric acid at 253 K. TEM observation was carried in a JEOL JEM-2100F microscope. High resolution TEM (HRTEM) images of the Fe₂Nb phase with the C14 structure were simulated using a multi-slice method [19].

Nano-indentation was performed with a Berkovich triangular pyramid indenter [20] using a HYSITRON Triboindenter at a maximum load of 40 mN. A minimum of 30 indentation tests were performed for each orientation in each of the three Laves phases at a constant loading rate of 2 mN/s and a holding time of 2s. All indents on the sample surface were observed by SEM in order to determine whether there were any cracks around the indent. We have excluded all hardness data where the indents were accompanied by microcracks on the sample surface. We note that, these microcracks were observed only in the Fe-rich binary Laves phase in the Fe-15Nb alloy.

In order to evaluate the compressive stress on the contact area of the sample surface with the indenter tip, we have assumed a model for elastic loading by a spherical indenter [21,22]. Considering the circular contact shape, the maximum contact pressure (compressive stress) σ is given by the following equation [23, 24],

$$\sigma = \left(\frac{6E_r^2}{\pi^3 R^2} \right)^{1/3} P^{1/3} \quad (1)$$

where P is the load, R is the radius of the indenter tip and E_r is the reduced modulus measured by nanoindentation. In the present study, the radius of the Berkovich indenter tip, R , is 400 nm, which was determined by fitting experimental load-displacement (P - δ) curves for elastic deformation (prior to pop-in) to the Hertzian contact on an elastic solid [21,22] given by the following equation,

$$P = \frac{4}{3} E_r \sqrt{R \delta^3} \quad (2)$$

Figure 3 shows a representative load-displacement curve for nanoindentation on

the Laves phase in a Fe-15Nb binary alloy together with theoretical curves calculated by Hertzian contact solution assuming an indenter tip radius R of 200, 400 and 600 nm. The experimental curve overlaps the theoretical curve obtained by assuming $R = 400$ nm till 3 mN in load (before pop-in). This confirms that the Berkovich tip used in our experiments is “blunt” with a radius of around 400 nm.

3. Results

3.1 Microstructure

Figure 4 shows the optical micrographs and the corresponding orientation color maps for Fe₂Nb Laves phase (C14 structure) of (a, b) Fe-15Nb, (c, d) Fe-15Nb-20Ni and (e, f) Fe-15Nb-40Ni alloys. The orientation along the surface normal direction is color-coded following the unit triangle. These alloys exhibit coarsened eutectic microstructures of γ -Fe and Laves phase with almost equal volume fractions. The Laves phase consists of a number of grains that are several hundred micrometers in size. The chemical compositions of the Laves phase are Fe-27Nb, Fe-27Nb-16Ni and Fe-26Nb-33Ni in the Fe-15Nb, Fe-15Nb-20Ni and Fe-15Nb-40Ni alloys, respectively [7,10]. The SEM observation revealed that some cracks were present within the Laves phase in the Fe-15Nb alloy and we speculate that these might be due to the γ - α martensitic transformation that occurs during the water quench. There are also no cracks within the Laves phase in the Fe-15Nb-20Ni, and the Fe-15Nb-40Ni alloys, possibly due to the γ -Fe phase being stabilized at room temperature.

Figure 5 shows TEM bright field images of the Laves phases with various compositions; these images roughly depict an area of 1.5 μm x 1 μm and are all taken with the same g vector, thereby enabling direct comparison. The binary

Laves phase in the Fe-15Nb alloy exhibits a featureless morphology with very few dislocations (**Fig. 5(a)**). However, in the Laves phase with Ni in solution, planar faults lying on the basal plane of the C14 structure were locally observed (**Fig. 5(b)**) and their density substantially increases by increasing the solute Ni content in the Laves phase to above 30%. The mean spacing of the planar faults is about 0.35 μm in Fe-15Nb-40Ni alloy (**Fig. 5(c)**), as reported elsewhere [25]. Note that these are widely extended faults with fault width being in excess of 5 μm ; in fact, these faults often extend to the central hole in the TEM thin foils.

Figure 6 shows a HRTEM image of the ternary Laves phase in the Fe-15Nb-40Ni alloy (in this alloy, the Laves phase has a composition of Fe-26Nb-33Ni), taken with the incident beam aligned along the [11-20] direction, together with a selected area electron diffraction pattern. In **Fig. 6(a)**, arrows indicate local irregularities in stacking on the basal plane of the C14 structure, corresponding to the planar faults observed by conventional TEM (**Fig.5(c)**). An enlarged portion of the lattice image corresponding to the fault-free region of the crystal is shown in **Fig. 6(b)** together with atomic positions determined by simulation superimposed on the image. It represents a stacking sequence of single layer (s) and triple layers (t, t') representative of the C14 structure (s t s t'...) [15,16]. **Figure 7** shows the crystal structure and stacking sequence of quadruple layers on the basal plane of the stoichiometric Fe_2Nb with the C14 structure. Here, the s layer is a kagome-net formed by Fe atoms (Fe2 sublattice), and the t layer consists of three 3^6 -nets, where one is formed by Fe atoms (Fe1 sublattice) sandwiched by two others formed by Nb atoms; t and t' are rotated 180° in the layer plane with respect to each other (**Fig.7 (b)**). The layer sequence (s t s t'...) corresponds well to the perfect region of the ternary Fe-26Nb-33Ni Laves phase (**Fig.6(b)**) although

atom site occupancy in these layers different from the stoichiometric binary C14 structure schematically illustrated in Fig. 7. The faulted region (Fig.6(c)) shows a different stacking sequence of s t's t'. This demonstrates that the planar faults on the basal plane in these ternary Laves phases correspond to a local difference in stacking sequence of the triple layers and is indicative of reduced C14 stability. The change in the stacking sequence is thought to be facilitated at the atomic level by the synchroshear process [15,16].

3.2 Nanoindentation

Figure 8 shows load-controlled nanoindentation load-displacement curves for the Fe₂Nb Laves phases with a fixed orientation that is close to the [10-11] as identified in the inverse pole figure. These curves almost overlap each other in the early stages of the test (load levels ranging from 2 to 5 mN), at which point, they exhibit a pop-in. In the Fe-26Nb-33Ni Laves phase, the pop-in occurs at a lower load as compared to the binary off-stoichiometric Fe-27Nb and the ternary Fe-27Nb-16Ni Laves phases. After pop-in, the curves shift relative to each other depending on the solute Ni content in the Laves phase. In particular, the Fe-26Nb-33Ni Laves phase exhibits a larger contact depth, which implies a lower hardness as measured by nanoindentation. Figure 9a-c shows inverse pole figures onto which is mapped the variation in hardness with the orientation of the indentation surface of the Laves phase in the three alloys. Fe-27Nb and Fe-27Nb-16 Ni Laves phases exhibit higher hardness than Fe-26Nb-33Nb. In the Fe-27Nb and Fe-27Nb-16Ni Laves phases, the hardness ranges from 13.3 to 13.8 GPa and is independent of orientation (Fig. 9(a,b)), whereas the Fe-26Nb-33Ni Laves phase exhibits an orientation dependence of hardness ranging from 11.1 to

13.4 GPa (**Fig. 9(c)**). We note here again that the average of more than 30 indentation values is presented for each orientation in this figure along with uncertainty ranges. An interesting observation by comparing **Figs 9a, 9b and 9c** is that for orientations where basal slip is NOT easy, the hardness is similar for all three alloys; for orientation where basal slip is feasible, the hardness is lower for the 33% Ni-containing ternary Laves phase. Thus, the lowest average hardness value of 11.1 GPa was measured along the [10-11] direction that makes an angle close to 45° to the basal plane normal.

SEM images of the nanoindents and the regions adjacent to them are shown in **Fig. 10** for the off-stoichiometric binary Fe-27Nb (a,b) and the ternary Fe-26Nb-33Ni (c,d) Laves phases. The indentation directions are nearly parallel to [6-3-32] in (a,c) and to [2-1-10] in (b,d), and these directions are shown in the inverse pole figure in **Fig. 10(e)**. Wavy traces can be observed around all indentations that correspond to the piling-up of materials due to plastic flow resulting from the nanoindentation [26]. In addition, clear slip traces can be observed around the indented region in the Fe-26Nb-33Ni Laves phase that has a surface normal of [6-3-32] (**Fig.10(c)**), whereas such slip traces are not readily apparent in the corresponding image for Fe-27Nb, (**Fig.10(a)**). No slip trace were observed for the [2-1-10] in either Laves phase (**Fig.10(b,d)**). Although slip trace analysis suggests predominantly basal slip, some non-basal slip traces were observed as well in the ternary hexagonal C14 Laves phase (**Fig. 10(c)**). These results directly indicate occurrence of slip in a ternary Laves phase with 33% Ni in solution when loaded in certain orientations but not in the corresponding binary Fe-rich Fe-27Nb Laves phase.

4. Discussion

Our study demonstrates that the ternary Laves phase with the composition Fe-26Nb-33Ni exhibits lower hardness than the off-stoichiometric (Fe-rich) binary Fe-27Nb Laves phase, both, at the nanometer-scale as well as at the micrometer-scale (as measured by Vickers indentation). This finding from the nanoindentation experiments confirms that the surrounding γ -Fe phase has negligible effect on the hardness that was previously measured by Vickers indentation. Both, from this study and from the systematic work done earlier [27], we note that even in the binary C14 Fe₂Nb Laves phase, the Fe-rich off-stoichiometric compound is softer than the stoichiometric counterpart. Furthermore, reasonably good agreement in hardness values are noted between the two studies for the binary stoichiometric and Fe-rich Fe₂Nb (9.8 GPa versus 9.3 GPa for stoichiometric Fe₂Nb and 9.1 GPa versus 8.2 GPa for the Fe-rich Fe₂Nb). Intriguing is the fact that substitution of Ni for Fe in the stoichiometric and Fe-rich Fe₂Nb (Fig. 1) produces only small changes in hardness up to about 20% Ni level; however, beyond that, in the Fe-rich Fe₂Nb, the hardness decreases rapidly and substantially with further increases in Ni substitution. Unfortunately, similar data for large Ni substitution in stoichiometric Fe₂Nb are not available.

Underlying reasons for progressive softening with deviations from stoichiometry in the case of the binary Fe₂Nb laves phase was not provided in the earlier study [27]. In binary AB₂ Laves phases, where A is the large atom and B is the smaller atom, deviation from stoichiometric composition to the B-rich side is accommodated by antisite defects where the excess small B atoms are thought to occupy the larger A atom sites in the triple layer; it is conceivable that this may affect the packing density of the triple layer and facilitate synchroshear. In an

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3 earlier study [16], a “vacancy-lubricated” kink motion model was suggested where
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5 the presence of a vacancy would facilitate kink motion that would then make
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7 synchroshear more viable; the replacement of the larger A atoms with a significant
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9 number of smaller B atoms in the triple layers could perhaps accomplish the same
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11 process. In this context it is worth noting that Fe-27Nb examined in this study
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13 significantly deviates from stoichiometry and roughly 20% of all the Nb atoms in
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15 the triple layer are replaced by the smaller Fe atoms. This will result in some free
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17 volume in the triple layer relative to the stoichiometric triple layer. The
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19 agglomeration of such free volume could facilitate the creation of vacancies if it
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21 reduces the internal energy of the structure and that might facilitate softening.
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26 It now appears that holding the Nb level constant at 27 at.% Nb and replacing the
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28 Fe with a significant amount of Ni leads to significant additional softening. In the
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30 off-stoichiometric ternary Laves phase that contains 33 at.% Ni but the same Nb
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32 level as the binary (27 at.% Nb) , if it is assumed that Ni simply replace Fe in the
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34 lattice, then, Ni will replace Fe atoms in the middle layer of the triple layer, the Fe
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36 atoms in the single Kagome layer as well as Fe atoms that are antisite defects and
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38 have substituted for Nb atoms in the triple layer (due to off-stoichiometry). How
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40 such complex structural modifications due to chemistry affect deformation
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42 mechanisms is not understood and requires atomic-scale computations that can
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44 examine core structure modification of the synchro-Shockley partial dislocation
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46 resulting from such alloying.

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48 Considering the solid solution softening by Ni in
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50 solution, one of the important findings in this study is the observation of pop-in at
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52 a small indentation depth of about 50 nm in the three Laves phases examined in
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54 this study. Pop-in is usually associated with onset of plasticity [22-24], and this
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56 suggests that dislocation nucleation and activation would occur underneath the
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3 nanoindentation. The plasticity would be closely related to the solid solution
4 softening of Laves phase and this is supported by the present results of slip traces
5 being observed on the basal plane on the indented surface (Fig. 10(c)). Previous
6 studies [15,16] have pointed out the occurrence of basal slip in Laves phase with
7 the C14 structure. Recently, the partial dislocation core structure associated with a
8 basal stacking fault in the C14 structure has been directly observed [28,29],
9 verifying the possibility of plastic deformation and polytypic transformations
10 occurring by synchroshear. Synchroshear requires two synchro-Shockley
11 dislocations bounding a planar fault to glide on two different levels inside the
12 triple layer with different Burgers vectors, for example, $1/3[10-10]$ and $1/3[-1010]$.
13 The passage of these dislocations can produce slip along $\langle 10-10 \rangle$ type directions
14 on a basal plane in the Laves phase.

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16 In order to examine the onset of plasticity in the Laves phase during
17 nanoindentation, the early stages of the load-displacement curves for binary
18 Fe-27Nb and ternary Fe-26Nb-33Ni Laves phases, obtained for different
19 orientations, are presented in Figure 11(a) and (b), respectively. In this study, we
20 have used the angle between the indentation direction and the basal plane normal
21 (ϕ) as a qualitative measure to identify the relative ease for basal slip. Thus, basal
22 slip is most favored when $\phi = 45^\circ$, whereas the deviation of ϕ from 45° is a
23 measure of the degree of difficulty in activating basal slip. We emphasize this
24 approach is qualitative; a more rigorous quantitative analysis has been described
25 by Li et al. [24] for the cases of single crystals of Ni and NiAl, where a parameter
26 called Indentation Schmid Factor is identified and the role of contact pressure is
27 given consideration in an anisotropic setting; however that analysis did not
28 consider dislocation dissociation and the presence of stacking faults in the

structure. **Table 1** summarizes ϕ , $|\phi - 45^\circ|$ and the contact pressure for the pop-in calculated by equation (1) for each of the orientations examined. The binary Fe-27Nb Laves phase exhibits pop-in at a fairly constant load level of about 3 mN that is independent of orientation (**Fig.11(a)**) as does the ternary Fe-27Nb-16Ni Laves phase. However, in the case of the ternary Fe-26Nb-33Ni Laves phase, pop-in load changes depending on orientation (**Fig.11(b)**) and becomes lower at lower degree of difficulty to activate basal slip ($|\phi - 45^\circ|$). The stress level ranging from 5.3 to 3.9 GPa might be equivalent to the high shear stress (about 2.4 GPa) on a basal plane of the ternary Laves phase micropillars measured by uniaxial compression test [18]; this is likely due to the lack of local dislocation sources [30] and reflects the stress for homogeneous nucleation of dislocations. The stress level for the pop-in is close to the theoretical shear strength and in the range of $G/30$ - $G/7$ (with G being the shear modulus) which is appropriate for homogeneous nucleation [31]. It was also shown in [18] that it is possible to plastically deform this ternary Laves phase by basal slip at room temperature at lower stresses (normal stress of ~800 MPa and a resolved shear stress on the basal plane of 315 MPa) provided dislocation sources are available. In the binary Laves phase, a constant pop-in stress independent of the orientation suggests the absence of a favorable operating slip mode. This result indicates that adequate Ni in solution can enhance basal slip in the Fe-rich Fe₂Nb Laves phase (in equilibrium with γ -Fe).

Another pertinent observation is the orientation dependence of hardness of the ternary Laves phase with 33% Ni in solution (Fe-26Nb-33Ni). The hardness was measured at a significant indentation depth of about 400 nm. Thus, the measured hardness would be governed by the collective effects of continued dislocation

nucleation, propagation and interaction with other pre-existing non-basal defects as well as activation of new basal and non-basal dislocation sources [21]. The hardness can be plotted as a function of the degree of difficulty to activate the basal slip system ($|\phi - 45|$), and this is shown in Fig. 12. The hardness of Fe-26Nb-33Ni Laves phase decreases from 13.4 to 11.1 GPa with decreasing the value of $|\phi - 45|$, whereas the hardness of Fe-27Nb Laves phase is almost constant at about 14 GPa independent of $|\phi - 45|$. This result demonstrates that the orientation dependence of hardness in Fe-26Nb-33Ni is closely related to the favorable orientation for basal slip. This finding is in line with the orientation-dependent pop-in load corresponding to the onset of plasticity. Furthermore, several slip traces along a basal plane of Fe-26Nb-33Ni Laves phase (Fig.10(c)) can provide direct evidence for the dislocation multiplication on the basal plane. Therefore, we conclude that more easily activated basal slip in the ternary Laves phase containing 33%Ni in solution is responsible for the softening of the Laves phase.

However, there is still the question of why Ni in solution facilitates the activation of basal slip more readily than in the off-stoichiometric (Fe-rich) Fe-27Nb binary C14 laves phase which already contains a high number of anti-site defects. One possible reason is a further decrease in Peierls barrier for synchroshear that might be facilitated by easier double kink nucleation and motion of the synchro-shockley dislocations [16] due to the presence of additional anti-site defects (Ni or Fe atoms replacing Nb sublattice site and Ni atoms replacing Fe in the Fe sublattice site). Additionally, as mentioned earlier, the influence of Ni on defect energies (stacking fault energy and dislocation core structure) needs to be understood to address this aspect satisfactorily. The presence of a higher density of stacking faults in the

ternary Fe-26Nb-33Ni Laves phase is indicative of a decrease in stacking fault energy in the presence of Ni and implies a decrease in the stability of the C14 structure toward perhaps other hexagonal polytypes such as the 4H and 6H structures ([16]). Further work is needed to better understand the chemical effect on structure, defect energies, structural stability and consequences on plasticity by basal slip.

5. Conclusions

In this study, we have observed defect structure and nano-hardness in Fe-rich Laves phase (in equilibrium with γ -Fe) with Ni in solution in Fe-Nb-Ni alloys. The conclusions are as follow:

(1) The binary Laves phase exhibits a featureless morphology with a low dislocation density, whereas the ternary Laves phase with 33 % Ni in solution includes many planar faults on the basal plane, which corresponds to a local change in the stacking sequence of the three 3^6 -nets (triple layer) of the C14 structure.

(2) The solute Ni atoms can decrease the hardness of Fe₂Nb Laves phase. The hardness of the binary and the ternary Laves phases with 18% Ni is almost constant and independent of orientation, whereas a ternary Laves phase with 33% Ni exhibits an orientation dependence of hardness that appears closely related to the ease of basal slip. Basal slip in the presence of a large amount of Ni in solution is the dominant contributor for the solid solution softening.

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Figure Captions

Figure 1: Change in Vickers hardness of Fe_2Nb Laves phases with stoichiometric and Fe-rich compositions as a function of the Ni content in solution. The hardness was measured using loads of 0.25N and 0.49 N.

Figure 2: Isothermal section of the Fe-Nb-Ni ternary phase diagram at 1473 K [10].

Figure 3: A representative nanoindentation load-displacement curve for the Laves phase in a binary Fe-15Nb alloy, together with theoretical curves calculated by Hertzian contact solution assuming an indenter tip radius R of 200, 400 and 600 nm.

Figure 4: Optical micrographs and corresponding orientation images for Fe_2Nb Laves phase (hexagonal C14) in (a, b) Fe-15Nb, (c, d) Fe-15Nb-20Ni and (e, f) Fe-15Nb-40Ni alloys, together with (g) the color-coded unit triangle of an inverse pole figure.

Figure 5: TEM bright field images of Fe_2Nb Laves phase in (a) Fe-15Nb, (b) Fe-15Nb-20Ni and (c) Fe-15Nb-40Ni alloys. Incident beam is nearly parallel to [11-20] direction.

Figure 6: (a) HRTEM image of Fe_2Nb Laves phase in the Fe-40Ni-15Nb alloy

showing planar faults on the basal plane, and enlarged HRTEM images of (b) the fault-free region and (c) the faulted region, where atom positions for Fe1 (orange), Fe2 (blue) and Nb (black) sublattice sites determined by simulation are superimposed. Incident beam is parallel to [11-20] direction.

Figure 7: (a) The C14 unit cell as applicable to stoichiometric Fe₂Nb, (b) 4 types of atomic layers parallel to the basal plane in the C14 structure, and (c) the <11-20> projection of the atomic structure. Yellow, blue and black spheres represent Fe1 site, Fe2 site and Nb site, respectively.

Figure 8: Representative nanoindentation load-displacement curves for the Laves phases with and without Ni in solid solution. In each case, the grain that was indented had a surface close to [10-11] that is identified in the inverse pole figure.

Figure 9: Variation of hardness with orientation of the indentation surface for (a) Fe-27Nb, (b) Fe-27Nb-16Ni and (c) Fe-26Nb-33Ni Laves phases mapped in inverse pole figure plots (Maximum load : 4.16×10^{-2} N).

Figure 10: SEM images showing the nanoindents and the surrounding region for two different indentation orientations: (a, b) Fe-27Nb and (c, d) Fe-26Nb-33Ni Laves phases (maximum load: 4.16×10^{-2} N), together with (e) the inverse pole figure showing the surface orientation. The indentation direction is nearly parallel to [6-3-32] in (a,c) and to [2-1-10] in (b,d).

Figure 11: Representative load-displacement curves for different orientations for the (a) binary Laves phase (Fe-27Nb), and (b) ternary Laves phase (Fe-26Nb-33Ni). ϕ indicates the angle between the indentation direction and the basal plane normal.

Figure 12: Change in hardness as a function of the degree of difficulty to activate the basal slip system ($|\phi - 45|$), using the angle between the indentation direction and the basal plane normal (ϕ).

Table 1: Angle between basal plane normal and indentation direction, load and corresponding stress for pop-in of the binary (Fe-27Nb) and ternary (Fe-26Nb-33Ni) Laves phases.

1. Introduction

Figure 1

2. Experimental procedure

Figure 2

2. Experimental procedure

Figure 3

3.1 Microstructures

Figure 4

3.1 Microstructures

Figure 5

3.1 Microstructures

Figure 6

3.1 Microstructures

Figure 7

3.2 Nanoindentation

Figure 8

3.2 Nanoindentation

Figure 9

3.2 Nanoindentation

Figure 10

4. Discussion

Figure 11

4. Discussion

Figure 12

4. Discussion

Table 1

	Angle between basal plane normal and indentation direction, ϕ (degree)	$ \phi - 45 $ (degree)	Pop in load (mN)	Pop-in stress (GPa)
Fe-27Nb	89	44	3.1	5.6
	6	39	3.2	5.6
	83	37	3.1	5.4
	74	29	3.3	5.6
	52	7	3.1	5.5
Fe-26Nb-33Ni	89	44	2.5	5.3
	86	41	2.4	5.1
	18	27	1.9	4.5
	60	15	1.5	4.2
	49	4	1.4	3.9