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The characterisation of second phases in the Zr-Nb and Zr-Nb-Sn-Fe alloys: A critical review

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Abstract

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The nature and evolution of the Fe environment in Zr-Nb and Zr-Nb-Sn-Fe systems is essential to alloy performance during corrosion, hardening and irradiation-induced growth. Unfortunately, there is ambiguity in the literature regarding the characterisation of secondary phases in these systems. The presence, or not, of Fe in β -Nb phase has been a source of disagreement. In ternary ZrNbFe intermetallics, identical compositions have been designated as $\text{Zr}(\text{Nb},\text{Fe})_2$ or $(\text{Zr},\text{Nb})_3\text{Fe}$. We show that while $\text{Zr}(\text{Nb},\text{Fe})_2$ is commonly reported, it is not always justified. The cubic phase $(\text{Zr},\text{Nb})_2\text{Fe}$ is easily identified, but its composition is more variable after low temperature heat treatments. We demonstrate the need for correlative approaches in the assessment of phase composition, crystallography and local Fe environment under different heat treatment regimes. Irradiation effects allow us to draw clues regarding phase designation, but there is diverse behaviour under irradiation due to initial phase composition, irradiation dose rate and temperature.

Table of Contents

1	Introduction.....	2
2	Nb terminal solid solubility in α -Zr	2
3	The β -Nb phase and “where the iron goes”	4
4	Ambiguity in the identification of binary Zr-Fe phases.....	7
5	The identification of ternary Zr-Nb-Fe phases.....	7
5.1	The $(\text{Zr},\text{Nb})_3\text{Fe}$ phase.....	11
5.2	The hexagonal $\text{Zr}(\text{Nb},\text{Fe})_2$ and cubic $(\text{Zr},\text{Nb})_2\text{Fe}$ phases	13
5.2.1	The hexagonal phase.....	14
5.2.2	The cubic phase	15
6	Irradiation Effects	16
6.1	The hexagonal phase	16
6.2	The cubic phase.....	18
7	Conclusions.....	18

1 Introduction

The corrosion and mechanical performance of Zr alloys is intrinsically related to the nature, morphology and behaviour of second phases and the underlying microstructure [1–9]. It is therefore essential to characterise second phases with clarity and consistency in order to accurately assess their evolving behaviour during the lifetime of nuclear components. Fe is known to be a critical element for many performance criteria and so its initial state in secondary phases and its evolution under alloy operating conditions must be studied with accuracy and precision, as only then can we elucidate a truly mechanistic understanding of deleterious phenomena. Such analysis lends itself to spatially resolved techniques, such as electron microscopy and related practises. Whilst synchrotron X-ray radiation studies have provided data on whether secondary phases exist in commercial alloys [10], wider quantitative X-ray data on phase structure is rare and, in X-ray studies, phase composition is calculated from alloy composition and not directly determined. The main source of data for the present review will therefore arise from electron microscopy and related techniques.

In commercial Zr-Nb and Zr-Nb-Sn-Fe alloys there are several phases that may exist, depending on alloy composition and thermomechanical history. The phases commonly reported in these alloys are α -Zr, β -Zr, β -Nb and ternary Zr-Nb-Fe phases, often designated $\text{Zr}(\text{Nb,Fe})_2$, $(\text{Zr,Nb})_3\text{Fe}$ or $(\text{Zr,Nb})_2\text{Fe}$. The secondary phases arise from a lack of Nb solid solubility in α -Zr and this topic is addressed in section 2. Whilst the composition and structure of the solid solution phases are generally consistent, the content of impurity Fe in β -Nb has been the cause for conflicting reports and will be assessed in section 3 of this review. The second section of this review concerns the ternary intermetallics. These systems contain a significant amount of all three constituents, but the data reported by different authors often does not match what is stated as the stoichiometric composition. Such conflicts have been the source of confusion in the characterisation of equilibrium phases in commercial Zr-Nb-(Sn)-Fe alloys and we aim to highlight and discuss the reasons for the ambiguity that currently exists. All

compositions from literature sources that are analysed in this work are presented in Figure 1, with alloy and heat treatment details analysed in the text and provided explicitly in the supplementary material. Please note that all phase compositions are provided in atomic per cent (at.%), unless otherwise stated.

2 Nb terminal solid solubility in α -Zr

In a fundamental study on the precipitation kinetics of the Zr-Nb system, parallel X-ray diffraction and thermoelectric power measurements were used to demonstrate the slow nucleation of secondary phases in such alloys, made even more sluggish by the addition of substitutional element Sn and faster by adding Fe or deformation prior to annealing [11]. This precipitation of the β -Nb phase and the ternary ZrNbFe phases in bulk α -Zr is primarily due to the low terminal solid solubility (TSS) of Nb in the α phase. The value of this TSS is, however, cause for some disagreement. In 2000, Canay et al. performed systematic electron microprobe chemical analysis on various ternary Zr-Nb-Sn alloys with composition Nb 1-3 at.% and Sn 0.8-1.6 at.% and quaternary Zr-Nb-Sn-Fe alloys with composition Nb 1 at.%, Sn 0.7-0.8 at.% and Fe 0.2-0.7 at.% [12]. Heat treatments were performed above the Zr-Nb monotectoid temperature and for times ranging 120-710 hr to achieve equilibrium conditions. The concentration of Nb found in the α -Zr was very low, <0.1 at.% in most cases where the alloy composition represented that of a commercial alloy. Nb concentrations in α -Zr only reached 0.3-0.7 at.% in alloys with high contents of Nb, Sn and that contain no Fe. However, it is very difficult to produce a Zr alloy with no Fe at all, as highlighted in a systematic TEM study of the phases present in Zr-Nb-Fe alloys [13]. In this other study, the authors demonstrated a significant effect of Fe on Nb TSS in Zr alloys and because Fe is almost always present as an impurity in Zr alloys it is very difficult to determine Nb TSS in the binary alloy. Interestingly, the authors observed no β -Nb phases within α -Zr when the alloy Nb content is 0.29 wt.% and did observe β -Nb when the Nb content was 0.49 wt.%. This leads to the conclusion that Nb TSS in α -Zr is in the range 0.29-0.49 wt.% at temperatures below the Zr-Nb monotectoid temperature (<600 °C), a value much greater than that suggested by Canay et al.

Figure 1 Ternary Zr-Nb-Fe diagram generated from data after [3,20–27,29,41–44,46,62–64]. All compositions are given in at.%. Marker style and colour relate to the phase designated by the authors of that publication.

In the ternary or quaternary alloys containing Sn, the α -phase Nb content in Zr-Sn-Nb alloys appears to be a function of the Sn concentration, whereas in binary Zr-Nb alloys the Nb content in the α -phase could be as high as 0.49 wt.%. In alloys with a high Sn content such as Excel alloy (Zr-3.5%Sn-0.8%Nb-0.8%Mo, wt.%) there is debatably no detectable Nb in the alpha phase (see discussion by Griffiths in [14]). Although values for the α -phase Nb content of 0.23 wt.% have been reported for Excel alloy [15], these values are not supported by the spectra shown in the paper and the accuracy of the quantitative analysis at such low values is therefore questionable. Nb content in the α -Zr phase of Excel has only been convincingly shown in alloys that are water quenched from between 690 and 876 °C, resulting in the retention of Nb in the α -Zr phase to between 0.37 and 0.59 wt.% [16]. With lower Sn

contents in ZIRLO™ and E635 alloys (1 wt.% Sn), the Nb content in the α -phase is measurably greater than for the Excel alloy (3.5 wt.% Sn). It appears that Sn, which is an α -stabiliser, reduces the solubility of Nb in the α -phase. At levels of Sn that apply to commercial Zr-Nb-Sn-Fe alloys (1 wt.% Sn), the Sn and Nb co-exist in solid solution [13]. The co-existence of Nb and Sn in solid solution in alloys such as E635 and ZIRLO™ (1 wt.% Sn) and the reduction in Nb in solid solution in Excel alloy with higher Sn content is one reason why Excel behaves more like the Zircalloys in terms of irradiation growth compared with other Nb-containing alloys [17]. The question of Nb TSS in α -Zr as a function of temperature therefore remains to be defined for the binary phase. It should be noted that all of the chemical composition work alluded to here was performed in a standardless manner, which is not

suitable for Nb quantification due to issues of X-ray fluorescence of Zr by Nb K_{β} . A quantitative energy-dispersive X-ray spectroscopy (EDS) study is therefore necessary to resolve this matter, or use of a method that does not suffer from fluorescence effects, such as atom probe tomography. The supersaturation of Nb in α -Zr has been demonstrated by the irradiation-induced precipitation of small Nb-rich phases in alloys Zr-1Nb and Zr-1Nb-0.1Fe (wt.%) [18].

3 The β -Nb phase and “where the iron goes”

The composition of β -Nb phase and whether or not it contains any Fe is subject to disagreement. We aim to assess and clarify the reasons for the contradictory data in this paper. The disagreement seems to be especially prevalent in commercial binary alloys and so we will begin there. The microstructural evolution of commercial Zr-2.5Nb (wt.%) under conventional heat treatment regimes is as follows. After quenching, cold-work and stress-relief, binary alloy Zr-2.5Nb (wt.%) contains both α -Zr and β -Zr phases. Further heat treatments below the Zr-Nb monotectoid temperature (~ 600 °C) result in the decomposition of the metastable β -Zr phase, which occurs via a two-stage process. In Zr-2.5 Nb pressure tubing at temperatures < 550 °C the first stage comprises decomposition of β -Zr to a Nb-enriched β -Zr phase and a Nb-depleted hexagonal ω -phase, where the Nb-enriched β -Zr phase takes two forms - one at α -Zr/ β -Zr grain boundaries and

one the untransformed β -Zr phase [19]. The second stage is the transformation of the Nb-depleted ω -phase into α -Zr and the Nb-enriched β -Zr into β -Nb phase. At temperatures close to the monotectoid temperature the formation of the ω phase is suppressed close to grain boundaries [10]. In advanced stages of decomposition the β -Zr phase transforms to the equilibrium state, β -Nb. The β -Nb can exist together with enriched β -Zr, and is also found in isolated grains and as precipitates at grain boundaries. Eventually the equilibrium state is achieved such that, in the case of the binary phases, there exists BCC β -Nb and HCP α -Zr that contains Nb in solid solution (< 1 wt.%). Interpretation of the binary phase states is often confounded by the presence of Fe that, like Nb, is a β -stabiliser. The Fe and Nb is enriched in the metastable phase states, and forms discrete ZrNbFe precipitates in advance of the complete decomposition of the β -Zr phase to β -Nb [10]. The compositional range for β -Nb is given from several studies in the ternary diagram of Figure 1 using data from [20–26], an analysis of which is shown in Figure 2. The diagram in Figure 1 represents the phases identified at room temperature, some of which may not be equilibrium phases. Figure 2a shows the full compositions reported for the Nb-rich precipitates, demonstrating predominantly zero concentration of Fe, but, in some cases, up to 4 at.% Fe (see Figure 1). Figure 2b shows the Zr:Nb atomic ratio of the reported with a modal value of ~ 0.125 .

Figure 2 An analysis of the compositional range of phases designated β -Nb. a) A frequency histogram of the Zr, Nb and Fe composition of those phases (NB: b) plotted on log scale as most contain 0 at.% Fe). b) A frequency histogram of the number of phases reported with a given ratio of Zr:Nb.

The presence of Fe in β -Nb is reported in model alloys that have significant Zr contents after long heat treatments at high temperatures above the Zr-Nb monotectoid temperature ($\sim 600^\circ\text{C}$) and above the lowest temperature for Zr-Fe β -phase stability ($\sim 775^\circ\text{C}$). One example is the $\text{Zr}_{60.6}\text{Nb}_{36.2}\text{Fe}_{3.2}$ phase in alloy $\text{Zr}_{41}\text{Nb}_{32}\text{Fe}_{27}$ after heating at 900°C for 500 hr [21]. This designation of β -Nb should be distinguished from the β -Nb that exists after heat-treatments below the Zr-Nb monotectoid. The Fe content in β -Nb below the Zr-Nb monotectoid is reported in commercial alloys but only convincingly in phases that were ZrNbFe ternary phases prior to irradiation that had undergone irradiation-induced Fe depletion resulting in a composition such as $\text{Zr}_{42}\text{Nb}_{50}\text{Fe}_8$, at.% [27]. Again, the description of the phase as β -Nb is somewhat ambiguous given that β -Nb has a Nb composition $\sim 85\%$ - 90% according to the binary Zr-Nb phase diagram [28]. The phases in Figures 1 and 2 that are reported with a Zr:Nb ratio ~ 0.1 , nominally β -Nb, with some non-zero Fe content are phases in model alloys that have been quenched from long heat treatments at 550 - 900°C [21,25], i.e. mostly above the Zr-Nb monotectoid temperature. Under commercial alloy heat treatments and compositions, the vast majority of studies report that there is no Fe detected in β -Nb [3,13,20,22,24,26,27,29–32]. Some early work did report Fe in β -Nb in commercial alloys and we will now take the opportunity to assess the validity of those claims in order to alleviate any confusion on the topic.

In 1991, Northwood et al. reported on the microstructure of Zr-2.5Nb (wt.%) [33]. Whilst the authors noted that their standardless Cliff-Lorimer approach to chemical quantification by energy dispersive X-ray spectroscopy (EDS) could result in an error in Fe measurement of as much as ± 25 at.%, they did not provide any evidence to support their claim that “there is a small amount of Fe and Cr in most of the β particles”. In fact, the only “typical” EDS spectrum that they provided for the β -Nb particles contained no Fe peak at all. Such a contradiction may be due to the method by which the data was collected; both thin foils and extracted particles were analysed but the authors were not clear in regard to which method their statements concerning Fe were based. Whilst the EDS spectrum provided in *Figure 6* of the publication by Northwood et al. is from a typical extracted particle and contains no Fe, Fe detection may be expected in thin foils; a recent publication from Francis et al. has clearly shown Fe segregation to the α -Zr/ β -Nb

interface in low-Sn ZIRLOTM [34], *Figure 3*. Therefore, depending on the position from which a single EDS spectrum is acquired and the size of the sampling electron probe, Fe may be detected in the foil at the interphase region. In such cases it is important to note that Fe will be segregated to the full 3D interfacial region and so some Fe may be detected in the interfacial region above or below the precipitate, depending on where the thin foil surfaces cut the precipitate. Here, 3D tomographic techniques (EDS, atom probe tomography) would be of use. Another source of an Fe X-ray signal is scattering from the pole-piece in an electron microscope. The magnitude of this Fe artefact increases proportionally with the number of backscattered electrons generated and, thus, the volume of material under examination. Therefore, errors of this kind will be minimised for extracted particles. Likewise, the Fe artefact can be accounted for with spatially resolved mapping protocols and quantification procedures for removing background signals.

In thin foils, site-specific segregation highlights the need for spatially resolved chemical information, especially as Fe scattering from the pole piece of TEMs can result in Fe peak artefacts. In Zr-2.5Nb (wt.%), a line scan was used to demonstrate Fe enrichment at the interphase region α -Zr/ β -Zr [19]. As enriched β -Zr ultimately transforms to β -Nb, this observation is consistent with that of Francis et al. [34]. Similarly, a line scan was used to demonstrate Fe enrichment at α -Zr/ α -Zr boundaries in Zr-2.5Nb-0.1Fe (wt.%) in the early 90s by Perovic et al. [35,36]. However, much of the early work by A. Perovic, V. Perovic and their associates has been an additional source of confusion regarding Fe in β -Nb. For instance, in the group’s first publication [35], Fe is reported in β -Nb but all β -Nb shown is on the α -Zr/ α -Zr boundaries. As these boundaries are also shown to be rich in Fe, their superposition with β -Nb may be misleading. Further, when quoting the content of Fe in the β -Nb particles, 0.86 wt.% Fe and slightly more in cold-worked stress-relieved material, the authors quoted the maximum Fe value for all of the particles studied and not the mean. They did not provide any indication of the number of particles studied or the composition of individual particles. In such circumstances a β -Nb particle containing up to 85 wt% Nb is listed in the same grouping as a “ β -Nb” particle containing up to 0.86 wt% Fe. Given the difficulty in accurate chemical analysis of small particles there is no way of knowing the true compositions of those phases

identified as β -Nb. The heat-treatment was 6h at 500 °C – insufficient to attain equilibrium [10]. This same maximum value was also quoted in a later publication by the group [37] on irradiated material and, whilst no Fe is detected in β -Nb post-irradiation, the authors state that the β -Nb in this irradiated state contains < 0.15 wt.% Fe according to their proposed detection limit. This is misleading on two counts: first, if no Fe is detected above background then no Fe should be reported; second,

such impressive detection limits are rarely quoted in the wider community, where minimum detection limits of 0.5 wt.% or even 1 wt.% are often attested to, especially for elements that have associated system artefacts, such as Fe. Spatially resolved chemical data is therefore necessary for convincing analyses, and, in the case of β -Nb, electron beam drift-correction is necessary as particles are often small and their interfacial region may contain segregated elements.

Figure 3 Fe segregation to the interfacial region α -Zr/ β -Nb, in the same body of work as [34]. Parts a), b) and c) show the Zr, Nb and Fe maps. Part d) shows these three maps overlaid. Part e) shows a line scan through the centre of the particle. Parts f), g) and h) show the EDS spectra from the interphase region, the α -Zr matrix and the centre of the particle, respectively.

One possible motivation for those early reports of Fe in β -Nb is to answer the question of what happens to the Fe after β -Zr decomposition, i.e. “where the iron goes”. Fe is a β -Zr stabiliser [38] and, indeed, Fe is reported in β -Zr, exemplified in Figure 1 with an Fe mean $\pm$ 1.96*std of 2.8 ± 2.1

at.%. The variability of Fe in β -Zr is therefore significant, but there is clearly some Fe in β -Zr. After the decomposition of β -Zr to Nb-enriched β -Zr and ω -phase (which is both Nb- and Fe-depleted relative to the parent β -Zr), there is a further transformation of Nb-enriched β -Zr to β -Nb, which, as has been

discussed, contains no Fe under commercial alloy heat treatment conditions. So, the question remains concerning the final residence of Fe. In the Zircaloy-2, Fe (and also Ni) is found at the vast majority of high-angle grain boundaries [39] and whilst we have already discussed the presence of Fe at interphase regions and at grain boundaries in the Zr-Nb system, it remains to be determined whether this is sufficient to account for the amount of impurity Fe present in Zr-2.5Nb (wt.%). Under β -Zr decomposition, the possibility of Fe dispersing into α -Zr and/or present as binary Zr-Fe intermetallics has been suggested by some [35], and ternary ZrNbFe intermetallics have been demonstrated by others [13,19]. The existence of ternary ZrNbFe intermetallics has been shown in quaternary Zr-Nb-Sn-Fe alloys such as ZIRLO™ [34,40], NSF-2 [41] and E635 [20,24,27,42–44], and has also been shown in Zr-1.25Nb (wt.%) [29] and in Zr-2.5Nb (wt.%), either standard pressure tubing containing Fe as an impurity, typically < 0.15 wt.% [45], or with added 0.1 and 0.5Fe (wt.%) [46]. An analysis of these ternary phases is to follow in section 5. As the Fe content in binary Zr-Nb alloys is very low, such ternary phases are scarcely reported but they may simply be small enough in number and size to have been missed in earlier studies with crude probe sizes and coarse detection limits. Modern TEM equipment affords much improved detectability and the oversights and corresponding ambiguities that have existed in the past should no longer be an issue.

4 Ambiguity in the identification of binary Zr-Fe phases

In an early characterisation of Zr-2.5Nb (wt.%) pressure tubing it was suggested that Fe exists in the form of ZrFe binary intermetallics, and an EDS spectrum was published to that effect in the energy range 5–19 keV [47]. Whilst binary ZrFe intermetallics are known in Zr-Sn-Fe-Cr type alloys [48], and have been demonstrated in Zr-Nb alloys of low Nb and Fe content [13], Zr₂Fe and Zr₂Si both have body centred tetragonal allotropes and so may be confused with one another when characterised by electron diffraction alone; indeed, it was later reported that Fe-coated zirconium silicides might be mistaken for binary ZrFe phases if Si is not explicitly looked for in the EDS spectrum [49] and it is therefore unfortunate that the authors of the initial study [47] did not publish the full spectrum to include the Si K α and K β emission lines at 1.7 and 1.8 keV. Further, the precipitate assumedly Zr₂Fe in

Figure 2 of that publication has a periphery that diffracts differently to the main body of the precipitate, suggesting that it is indeed coated with another phase or region. The mis-identification of the Zr₂Fe then impacts the future interpretation of the Mössbauer signals assigned to this phase in that study. The presence of binary ZrFe intermetallics in Zr-2.5Nb (wt.%) was reported again at a similar time [33], but the diffraction patterns provided in that study did not correlate well with the indexing and no chemical analysis was provided. Woo and Griffiths have well-characterised the appearance of various phases in “binary” Zr-Nb systems with impurities of Fe, and, to a lesser extent, Cr, Ni, Cu and W [13]: binary ZrFe and ZrSi phases are present at low Nb and Fe contents (< 0.2 wt.% Nb and < 24 wt. ppm Fe) and higher Nb and Fe alloys predominantly nucleate ZrNbFe intermetallics and the β -Nb phase. It is therefore advisable to publish the full 0–20 keV EDS spectrum when reporting the existence of binary ZrFe phases in such alloys to remove the suspicion of silicides. In recent work, heavy ion Kr²⁺ irradiation of alloy Zr-2.5Nb (wt.%) has resulted in the irradiation-induced decomposition of the β -Zr phase to ω -phase and has shown the presence of Fe-rich phases post-irradiation [50], thought to be binary ZrFe in nature. However, as yet, a quantitative analysis on these precipitates remains to be performed, and their nucleation may be related specifically to irradiation and not necessarily as an irradiation-assisted evolution towards the phases of thermodynamic equilibrium. It is likely that their nucleation is irradiation-induced, as binary Zr₃Fe is known to be relatively resistant to irradiation [51,52] and is known to nucleate in Zircaloy-4 after neutron irradiation [53] and in Zircaloy-2 after proton irradiation [54]. As ternary intermetallics are the most likely candidate for where the Fe resides in Zr-2.5Nb (wt.%) after β -Zr decomposition, their characterisation will be assessed in the following section.

5 The identification of ternary Zr-Nb-Fe phases

Similarity in the composition of phases can easily result in confusion regarding stoichiometric designation. The early characterisation of intermetallic ZrNbFe phases took place in the USSR, where researchers identified a phase with a composition of approximately Zr₅₂Nb₁₀Fe₃₈ (at.%) [55,56]. This phase was referred to as the “T” phase, possibly due to the Russian “троичный” for

“ternary”, and the crystal structure was not determined at that time. A wider compositional range of ternary ZrNbFe phases has been reported since. Some insight into the nature of the ZrNbFe phases can be obtained from work on the binary ZrFe alloys. In a comprehensive assessment of binary ZrFe phases, Stein et al. have noted four phases, of which we shall be concerned with three: ZrFe_2 (cubic or hexagonal), Zr_2Fe (tetragonal or face-centred cubic) and Zr_3Fe (orthorhombic) [57]. It is conceivable that the ZrNbFe phase diagram may also contain a similar variation of phases with the added complication that the slower diffusing Nb will result in metastable states that would complicate the final structure when a given alloy is subjected to multiple heat treatments. In the ternary equivalents,

we may expect Nb to replace some of the Zr due to the similarities between these two elements in terms of their atomic mass (Zr 91.22 and Nb 92.91 g mol⁻¹) and atomic radii (Zr 0.206 and Nb 0.198 nm, theoretical). Surprisingly, however, most reports of ternary ZrNbFe phases state that Nb replaces some of the Fe to produce the phase $\text{Zr}(\text{Nb},\text{Fe})_2$ and this phase is commonly referred to as a Laves phase. This replacement of Fe by Nb instead of Zr by Nb has lead to conflicting reports in terms of phase designation for similar phase compositions. In one of the earliest reports identifying the phases in the Zr-Nb-Fe ternary system by Kanematsu [58] the Nb was assumed to substitute for Zr in the equivalent phases of the ZrFe binary.

Figure 4 An analysis of the compositional range reported for the ternary Zr-Nb-Fe phases a) hexagonal and b) cubic. Data taken from Figure 1.

The compositions commonly reported for the ternary ZrNbFe phases are usually designated as either hexagonal $\text{Zr}(\text{Nb},\text{Fe})_2$ or cubic $(\text{Zr},\text{Nb})_2\text{Fe}$. The chemical range of these designations is shown in frequency histograms in Figure 4. This figure demonstrates why the hexagonal and cubic phases are easy to distinguish; the cubic phase in Figure 4b has well-defined and separate constituent compositions, however, for the hexagonal phases in Figure 4a there is significant overlap in compositions. This overlap in the hexagonal phase composition has resulted in ambiguity in its designation as either $\text{Zr}(\text{Nb},\text{Fe})_2$ or $(\text{Zr},\text{Nb})_3\text{Fe}$ [19]. This ambiguity is shown in Figure 1; the reported $(\text{Zr},\text{Nb})_3\text{Fe}$ composition is at the very boundary of the very large range of compositions reported as

$\text{Zr}(\text{Nb},\text{Fe})_2$ by others. These two phase designations are chosen by authors to reflect their binary equivalents, Zr_3Fe and ZrFe_2 . It is noteworthy that Zr_2Fe and ZrFe_2 are the two main intermetallic phases above 775 °C, whereas Zr_3Fe and ZrFe_2 are the two main intermetallic phases below 775 °C according to Stein et al. [57]. When assessing whether or not the ZrNbFe phases identified in any particular study are consistent with the Zr-Fe phase diagram one needs to know whether the final heat treatment is above or below 775 °C, or some similar phase boundary temperature for the Zr-Nb-Fe ternary. Whilst $\text{Zr}(\text{Nb},\text{Fe})_2$ has been reported in the majority of cases, many of those compositions reported also fit well with $(\text{Zr},\text{Nb})_3\text{Fe}$ stoichiometry. In Figure 5a and Figure 5b we plot frequency

histograms of some atomic ratios for all hexagonal phases reported. In Figure 5a we pair Nb with Fe and Cr to assess the suitability of $\text{Zr}(\text{Nb,Fe})_2$ designation and in Figure 5b we pair Nb with Zr to assess the suitability of $(\text{Zr,Nb})_3\text{Fe}$ designation. We can see that the ratio $(\text{Nb}+\text{Fe}+\text{Cr}):\text{Zr}$ is frequently < 2 and that the ratio $(\text{Zr}+\text{Nb}):(\text{Fe}+\text{Cr})$ is most

frequently between 2 and 3; hence the confusion in stoichiometric designation. It is likely, and often stated, that most researchers prefer to label a phase containing Zr, Nb and Fe as hexagonal Laves $\text{Zr}(\text{Nb,Fe})_2$ because stacking faults are also often observed, however it is not clear that this is a defining condition for this phase.

Figure 5 An analysis of the ratio of ternary constituents in analogy to binary equivalents by pairing Nb with either the light transition elements Fe, Cr or with Zr; for the hexagonal phase Nb coupled with a) Fe, Cr and b) Zr and for the cubic phase with Nb coupled with a) Fe, Cr and b) Zr. Data taken from Figure 1.

An analysis of the relationships between phase composition and alloy composition or heat treatment type may help us to deduce correct stoichiometry. In Figure 6 we plot the composition of a phase against the atomic ratio Fe:Nb in the alloy. In part a), b) and c) the Zr, Nb and Fe composition for the phase designated by authors as hexagonal $\text{Zr}(\text{Nb,Fe})_2$ is plotted in four ways: those alloys heat treated either above or below the

monotectoid temperature for β -Zr decomposition ($\sim 600^\circ\text{C}$) and those that have a phase composition ratio $(\text{Zr}+\text{Nb}):(\text{Fe}+\text{Cr})$ either $<$ or ≥ 2.5 (limit chosen as half way between 2 and 3), i.e. how well the phase fits with stoichiometry $(\text{Zr,Nb})_3\text{Fe}$ but was designated $\text{Zr}(\text{Nb,Fe})_2$ by the authors (note that Cr, when reported, is added to Fe for simplicity). From Figure 6 b) we can see that the Nb content in the phase is inversely proportional to the Fe:Nb in the

alloy and from Figure 6 c) that the Fe content in the phase is directly proportional to the Fe:Nb in the alloy. From Fe:Nb in part a) we see that the Zr content in the phase does not change with respect to the Fe:Nb in the alloy. Therefore, the phase Fe:Nb is directly proportional to the alloy Fe:Nb. However, such a trend is only observable when the ratio Fe:Nb

in the alloy exceeds ~ 0.5 , which is much larger than in commercial alloy systems. It has been noted that “...the stoichiometry of the ternary intermetallic phases was nearly independent of the alloy compositions” [59] but this likely refers to the Zr:(Fe+Nb) ratio, which is indeed constant as shown here in Figure 6 (a).

Figure 6 An analysis of the variation in phase composition with respect to alloy Fe:Nb ratio, both above and below the monotectoid temperature for β -Zr phase decomposition; for the hexagonal phase in a) Zr, b) Nb and c) Fe and for the cubic phase in d) Zr, e) Nb and f) Fe. Data taken from Figure 1.

Whilst we may suggest that a constant Zr phase content suggests a constant Zr:(Nb+Fe+Cr) ratio and therefore the appropriate designation $\text{Zr}(\text{Nb},\text{Fe})_2$, the Zr content remains significantly scattered in the range 29-43 at.% Zr with one outlier at 55.2 at.% Zr. This is a significant point because Laves phases, a family of which $\text{Zr}(\text{Nb},\text{Fe})_2$ is often reported to be, commonly have strict stoichiometries AB_2 with the A composition varying by 2-3 at.% [60]. Although the Zr compositional range in Zr-Fe systems this variation is known to be wider than this, the Zr composition range for the reported $\text{Zr}(\text{Nb},\text{Fe})_2$ is extraordinarily wide. This may reflect a tendency for matrix overlap when analysing the composition of small particles embedded in a Zr-rich matrix but only accentuates the uncertainty in the data that is reported.

From the data in Figure 6, 32% of compositions have a ratio $(\text{Zr}+\text{Nb}):(\text{Fe}+\text{Cr}) \geq 2.5$, i.e. have an Fe content ≤ 28.5 at.% and therefore fit well with stoichiometry $(\text{Zr},\text{Nb})_3\text{Fe}$. This is more prevalent below the monotectoid temperature than above it; 34% of reported compositions fit well with $(\text{Zr},\text{Nb})_3\text{Fe}$ below the monotectoid and above the monotectoid only 15%, highlighting the importance of investigations both above and below this temperature. In Figure 6 parts d), e) and f) this analysis is repeated for a different phase: cubic $(\text{Zr},\text{Nb})_2\text{Fe}$, designated by authors in analogy to the binary Zr_2Fe . For this phase, only 3% of phase designations better fit $(\text{Zr},\text{Nb})_3\text{Fe}$ (4% below the monotectoid and 0% above), and so the ambiguity in stoichiometry designation is not so much of a problem with the cubic phase. The $(\text{Zr},\text{Nb})_2\text{Fe}$ is relatively easy to identify as it is cubic, as opposed to hexagonal, and contains characteristically low Nb

content. The $\text{Zr}(\text{Nb,Fe})_2$ is always reported as hexagonal and the $(\text{Zr,Nb})_3\text{Fe}$ has been reported as both orthorhombic and hexagonal (which is also orthorhombic). Therefore, when an investigator observes a hexagonal structure with a reasonably high Nb content they may simply assume $\text{Zr}(\text{Nb,Fe})_2$ phase. Whilst this may not necessarily be incorrect, there are conflicting reports. The following is a detailed and critical assessment of phase designation in relation to these reports.

5.1 The $(\text{Zr,Nb})_3\text{Fe}$ phase

It is important that authors provide as many details as possible in regards to their analysis, as investigations of small volumes are easily unrepresentative and are prone to errors. Second phases in commercial Zr alloys generally have a diameter on the order of < 100 nm. As such, analysis techniques with high spatial resolution are necessary for their characterisation and transmission electron microscopy (TEM) has such capability. However, sample preparation is key; the matrix in which the second phases are imbedded may contribute to the chemical data obtained by energy dispersive X-ray spectroscopy (EDS) or data relating to crystallography by the recording of electron diffraction patterns (DPs). To alleviate this issue, one must be specific in the number of

particles studied and their location with respect to the foil edge, such as those studied by Tian et al., shown here in Figure 7a for both β -Nb and ternary Zr-Nr-Fe phases in an α -Zr matrix [26] and, similarly, other examples that explicitly show the particle being reported upon, such as the ternary ZrNbFe particle in Figure 7b [19]. These examples, whilst explicit, would benefit from spatially resolved data in the form of line scans or mapping, see for example the maps shown in [45], used to identify both the β -Nb and $(\text{Zr,Nb})_3(\text{Fe,Cr})$ phases in Zr-2.5Nb pressure tubing heat-treated below the monotectoid temperature. Oversights in this practise make it difficult to assess the validity of compositions such as “50Zr-30Nb-20Fe (%)” [29], in which the particle number and location details were not given and the percentage type was not provided. If atomic per cent then this refers to a stoichiometry that could be written $(\text{Zr,Nb})_4\text{Fe}$, which has no binary equivalent and has not been reported elsewhere. This may point towards an excess of Zr signal from the matrix. If the composition is weight per cent then when converted to atomic per cent the stoichiometry is closer to $(\text{Zr,Nb})_3\text{Fe}$. This stoichiometric designation has been reported to some extent and will be assessed here.

Figure 7 a) Tian et al. show the number of particles studied and their location with respect to the foil edge when reporting their quantified compositions [26]. b) Griffiths et al. explicitly show the ternary particle under discussion and its location with respect to the α/β interface.

To avoid excess matrix contribution to chemical quantification, Ng-Yelim, Woo and Carpenter used extraction replicas to remove all matrix contribution for the characterisation of second phase particles in, amongst others, alloy Zr-2.5Nb (wt.%) with additions of either 0.1Fe or 0.5Fe (wt.%) [46]. The authors compared their compositional analysis to a stoichiometric alloy of $\text{Zr}_{1.5}\text{Nb}_{1.5}\text{Fe}_1$ (presumably at.%), which they determined by EDS as $\text{Zr}_{37.5}\text{Nb}_{37.5}\text{Fe}_{25.0}$ (at.%). The authors designated this phase $(\text{Zr,Nb})_3\text{Fe}$. Whilst this assignment may seem appropriate as an analogue to the binary orthorhombic Zr_3Fe [57,61], no crystallographic analysis was provided for this stoichiometry alloy. The only reported electron diffraction work was for the extracted particles in the commercial-type alloys, which were found to have the hexagonal crystal structure with lattice parameters $a = 0.54$, $c = 0.88$ nm and the following mean compositions: $\text{Zr}_{35.7}\text{Nb}_{40.9}\text{Fe}_{23.4}$ (at.%) for the 0.1Fe alloy and $\text{Zr}_{37.8}\text{Nb}_{40.2}\text{Fe}_{22.0}$ (at.%) for the 0.5Fe alloy (note that the Cr content has been added to the Fe content for clarity) [46]. Whilst the compositions of the extracted particles almost match that of the $\text{Zr}_{1.5}\text{Nb}_{1.5}\text{Fe}_1$, there was no direct crystallographic comparison shown and there was no report of whether the $\text{Zr}_{1.5}\text{Nb}_{1.5}\text{Fe}_1$ was thoroughly analysed for multiple phases. In agreement with Ng-Yelim et al. [46], Motta et al. reported hexagonal $(\text{Zr,Nb})_3\text{Fe}$ in an alloy with the same stoichiometry $\text{Zr}_{1.5}\text{Nb}_{1.5}\text{Fe}_1$ (presumably at.%) via EDS and electron diffraction, although no spectra or patterns were shown in that particular publication [62]. The lattice parameters reported for the hexagonal phase found in that alloy were in good agreement with those of the extracted particles in Ng-Yelim et al.: $a = 0.54$ and $c = 0.88$ nm [62].

Nikulina et al. reported two phases in alloy E635 (Zr-1Nb-1Sn-0.4Fe (wt.%)), which were attributed to the following stoichiometries: the $(\text{Zr,Nb})_3\text{Fe}$ similar to that of Ng-Yelim et al. and $\text{Zr}(\text{Nb,Fe})_2$ [42]. Although the authors only gave a single compositional range to include both phases and gave no indication of the number of particles studied or their location with respect to the foil edge, and so we cannot discuss their compositions here, they did provide two crystallographic identifications by electron diffraction: orthorhombic $(\text{Zr,Nb})_3\text{Fe}$ with $a = 0.88$, $b = 0.33$, $c = 1.10$ nm and hexagonal $\text{Zr}(\text{Nb,Fe})_2$ with $a = 0.51$, $c = 0.83$ nm. Therefore, in comparison to Ng-Yelim et al. [46] and Motta et al. [62], Nikulina et al. gave the $(\text{Zr,Nb})_3\text{Fe}$ stoichiometry but with a different crystal structure

and a different stoichiometric compound $\text{Zr}(\text{Nb,Fe})_2$ with the same structure as Ng-Yelim et al.'s [46] and Motta et al.'s [62] $(\text{Zr,Nb})_3\text{Fe}$.

The binary phase Zr_3Fe is Re_3B -type orthorhombic with lattice parameters $a = 0.332$, $b = 1.100$, $c = 0.882$ nm [57], in excellent agreement with Nikulina et al.'s structure determination for $(\text{Zr,Nb})_3\text{Fe}$ [42]. However, the two phase designations by Nikulina highlights the confusion between the designation $(\text{Zr,Nb})_3\text{Fe}$ and $\text{Zr}(\text{Nb,Fe})_2$. The confusion of $(\text{Zr,Nb})_3\text{Fe}$ and $\text{Zr}(\text{Nb,Fe})_2$ would occur for a composition of something surrounding $\text{Zr}_{33}\text{Nb}_{42}\text{Fe}_{25}$ (at.%), which is at the edge of the range reported in the wider literature (see the central region of Figure 1) and 32% of reports of $\text{Zr}(\text{Nb,Fe})_2$ in the literature would fit well with the designation $(\text{Zr,Nb})_3\text{Fe}$ (see Figure 6 a) for phase $(\text{Zr+Nb})\text{:Fe} > 2.5$). Importantly, there have been reports that show Nb to have very low solubility in the binary phase Zr_3Fe (0-2 at.%, depending on alloy and heat treatment) [63]. Therefore, we may not expect $(\text{Zr,Nb})_3\text{Fe}$ to be orthorhombic, although orthorhombic $(\text{Zr,Nb})_3\text{Fe}$ has been noted by the same group both in E635 [42] and in E125 Zr-2.5Nb (wt.%) [20]. However, as no diffraction characterisation was evidenced in those works we may assume that this phase was not studied in detail.

The lattice parameter of hexagonal $(\text{Zr,Nb})_3\text{Fe}$ reported by Ng-Yelim et al. [46] and Motta et al. [62] is in agreement with the hexagonal $\text{Zr}(\text{Nb,Fe})_2$ phase of Nikulina et al. [42], and indeed with many other groups for the reported $\text{Zr}(\text{Nb,Fe})_2$ phase [20,21,23,27,44,64], a more in-depth discussion of which is to follow. It may be the case that the hexagonal [46,62] and orthorhombic [42] lattices are confused because a hexagonal crystal is indeed orthorhombic. However, the lattice parameters noted by the relevant groups are significantly different for this to be a likely source of confusion. It may be the case that the phase designation $\text{Zr}(\text{Nb,Fe})_2$ is assigned to a phase if it simply appears hexagonal, even though it may fit better with stoichiometric designation $(\text{Zr,Nb})_3\text{Fe}$. However, the designation as $(\text{Zr,Nb})_3\text{Fe}$ has not been reported since Averin et al. in 2000 in Zr-2.5Nb and has never been explicitly characterised with scrutiny by modern methods. The very existence of this phase, its compositional range, its structure, its formation under different heat treatments, its thermodynamic metastability in comparison to other, more well known, phases and its behaviour under irradiation all remain open questions to date.

In summary, it is either the case that there is a single hexagonal ternary phase with a wide compositional range or it is the case that there are two phases, possibly both hexagonal, with narrower compositional ranges and with the Nb associated with either the Fe, as in $\text{Zr}(\text{Nb},\text{Fe})_2$, or with the Zr, as in $(\text{Zr},\text{Nb})_3\text{Fe}$. It is noteworthy that Kobylansky et al. describe certain precipitates as $(\text{Zr},\text{Nb})_2\text{Fe}$ and also state that the Fe content is 25 at% after irradiation in Table 11 of [43], which may also indicate that the phase has reached equilibrium at the irradiation temperature (about 330 °C), and is a good example of how such confusion in stoichiometric designation can arise. Indeed, the composition of Laves phases is known to be narrow, but heat treatments are likely to play a significant role in the compositions obtained in ternary phases. Whilst most characterisation of ternary ZrNbFe phases have reported stoichiometries of $\text{Zr}(\text{Nb},\text{Fe})_2$ and $(\text{Zr},\text{Nb})_2\text{Fe}$ (see the following section for a discussion of this latter phase), the effect of heat treatments above and below the monotectoid temperature for β -Zr decomposition has not been studied in detail with respect to varying alloy composition. We show this effect in Figure 6 and more detailed, systematic, correlative chemical-structural studies of the same alloys above and below the monotectoid are necessary for better phase identification in Zr-Nb-Fe ternary systems. The question remains as to whether the $(\text{Zr},\text{Nb})_3\text{Fe}$ phase, reported prior to 2000, exists and has simply been designated $\text{Zr}(\text{Nb},\text{Fe})_2$ by recent tradition. It is the present authors' opinion that there is a habit within the literature to simply assign a phase as $\text{Zr}(\text{Nb},\text{Fe})_2$, even if the composition does not reflect this stoichiometry. Therefore, a line of enquiry is needed to directly resolve this issue, preferably with investigation into Fe, Nb and Zr local environments in order to assess whether we should associate the Nb with the Fe or the Zr for designation as $\text{Zr}(\text{Nb},\text{Fe})_2$ or $(\text{Zr},\text{Nb})_3\text{Fe}$, respectively.

5.2 The hexagonal $\text{Zr}(\text{Nb},\text{Fe})_2$ and cubic $(\text{Zr},\text{Nb})_2\text{Fe}$ phases

In more recent years, extensive study of model ternary Zr-Nb-Fe alloys by Argentinian groups [21,23,63–65] and French groups [3,22,25,66] have reported the existence of two dominant ternary ZrNbFe phases: the hexagonal $\text{Zr}(\text{Nb},\text{Fe})_2$ and the face-centred cubic $(\text{Zr},\text{Nb})_2\text{Fe}$. These comprehensive characterisation studies have included many alloy compositions and have been assessed with various analytical techniques, sometimes combining

Mössbauer spectroscopy for Fe coordination environment with X-ray diffraction for the identification of crystal structure and the measurement of lattice parameters and chemical quantification by wavelength dispersive spectroscopy in the electron microprobe or energy-dispersive X-ray spectroscopy in the TEM. Whilst these studies have been comprehensive in the range of alloys considered, the work is often in a single temperature range (either above or below the monotectoid for β -Zr decomposition). Further, because the test matrix is so large in these studies, the compositions reported are a single measurement for an alloy/heat treatment condition; no indication is given in regards to compositional variation or error in the measurement itself. Although it is important to obtain data from a large number of particles for good statistics to assess phase compositional range (see the work of Harte et al. in [67] for the compositional range of precipitates in Zircaloy-2 as a function of proton and neutron irradiation dose), it is more important to perform accurate and precise measurements through good practise; doing so will allow proper comparisons between different studies and reliable conclusions. Regardless of the lack of any compositional range in these reports, the volume fraction of reported $\text{Zr}(\text{Nb},\text{Fe})_2$ relative to $(\text{Zr},\text{Nb})_2\text{Fe}$ has been shown as dependent on alloy composition [64] and the importance of long annealing times to reach equilibrium phase compositions has been demonstrated, especially at low annealing temperatures [3,22], e.g. up to 20,000 hr at 400 °C. This is important when slow diffusers such as Nb are involved in the phase composition [66]. Long heat treatments are rarely performed in commercial alloys due to the relative importance placed upon control of grain size and stress relief. Therefore, non-equilibrium compositions should be expected in commercial systems. Of course this can result in confusion in regards to stoichiometric assignment.

Due to the ambiguity in stoichiometric designation of compositions surrounding $\text{Zr}_{33}\text{Nb}_{042}\text{Fe}_{25}$ (at.%), already discussed in the introduction to section 5 and within section 5.1 as either $\text{Zr}(\text{Nb},\text{Fe})_2$ or $(\text{Zr},\text{Nb})_3\text{Fe}$, we will refer to the phases commonly designated as $\text{Zr}(\text{Nb},\text{Fe})_2$ as hexagonal and $(\text{Zr},\text{Nb})_2\text{Fe}$ as cubic, with the understanding that the hexagonal phase is sometimes ambiguous in its stoichiometry.

5.2.1 The hexagonal phase

The differences in the compositional range for the phases designated as hexagonal and cubic has been demonstrated in Figure 1 and Figure 4 and the conflict between designation of a hexagonal phase as $\text{Zr}(\text{Nb},\text{Fe})_2$ or $(\text{Zr},\text{Nb})_3\text{Fe}$ is shown in Figure 1 and Figure 6. However, Figure 1 and Figure 6 demonstrate the relative consistency of the Zr content relative to that of Nb and Fe, suggesting a greater likelihood of $\text{Zr}(\text{Nb},\text{Fe})_2$ in most cases. In Figure 6 we can also see that the Fe and Nb content of the hexagonal phase is correlated to the atomic ratio Fe:Nb in the alloy, and, likewise, the cubic phase content of Zr and Nb ratio is correlated to the alloy Zr:Nb. In Figure 5 we present frequency histograms of the two different possible Nb couplings for both the hexagonal and cubic phases. In Figure 5 a) and b) for the hexagonal phase we show the phase atomic ratio $(\text{Nb}+\text{Fe}+\text{Cr}):\text{Zr}$ and $(\text{Zr}+\text{Nb}):(\text{Fe}+\text{Cr})$ to demonstrate that the ratio $(\text{Nb}+\text{Fe}+\text{Cr}):\text{Zr}$ is generally < 2 and that the average $(\text{Zr}+\text{Nb}):(\text{Fe}+\text{Cr})$ lies between 2 and 3. The cubic phase shows better adherence to stoichiometry but there remains significant variation between measurements.

A summary of the mean $\pm 1.96*\text{std}$ is given in Table 1. For the hexagonal phase we can see from Table 1 that the variation in Nb and Fe measurement is almost three times that for Zr, reinforcing the stoichiometric formula $\text{Zr}(\text{Nb},\text{Fe})_2$. There are some studies that unfortunately add confusion through a lack of clarity in assigning a phase as $\text{Zr}(\text{Nb},\text{Fe})_2$ or $(\text{Zr},\text{Nb})_3\text{Fe}$; several possible crystallographic solutions, hexagonal, tetragonal and orthorhombic have been provided in a single publication with no indexed diffraction patterns and only a single compositional range reported [27,30]. Other publications have simply stated that there are “mainly” $\text{Zr}(\text{Nb},\text{Fe})_2$ in alloy E635 but have not provided any characterisation or referred to any minor fraction of secondary phase [31]. There has also been confusion in phase designation in alloy NSF-2 after an incomplete report of the composition of a phase and its designation as $(\text{Zr},\text{Nb})\text{Fe}_2$ [41]. This phase was indexed as hexagonal but there was confusion in the reporting of the composition and so no further analysis can take place here. There is evidence for the existence of the hexagonal phase over a wide alloy compositional range; $\text{Zr}(\text{Nb},\text{Fe})_2$ has been reported in alloys containing as little alloying elements as alloy $\text{Zr}_{99.78}\text{Nb}_{0.17}\text{Fe}_{0.05}$ (at.%) [3] to those containing as much as alloy $\text{Zr}_{40}\text{Nb}_{50}\text{Fe}_{10}$ or $\text{Zr}_{30}\text{Nb}_5\text{Fe}_{65}$ (at.%) [23] and there are several

studies that show the presence of the hexagonal phase in commercial alloys with various Fe additions [24,27] and in a wide range of model alloys [3,21–23,64]. This alloy compositional range is reflected in the wide compositional range of the phase itself.

The hexagonal phase has been widely reported as (C14) MgZn_2 -type crystallography, which is a Laves phase structure and is often referred to as such. However, Stein et al.’s data indicate that the parent ZrFe_2 phase in equilibrium at temperatures $< 600^\circ\text{C}$ is cubic [57]. We may study the variation in lattice parameter as a function of chemical content from literature data in which parallel chemical and crystallographic analyses were performed. In Figure 8a and Figure 8b we plot phase chemical content as a function of unit cell volume for the hexagonal and the cubic phase, respectively. Stark differences are clear between the two phases in that the hexagonal phase unit cell volume is much more sensitive to changes in composition. We may expect the unit cell to increase with an increase of Nb content and decrease in Fe due to an atomic radii argument. Whilst this may be true for both the assignment of the hexagonal phase as $\text{Zr}(\text{Nb},\text{Fe})_2$ or $(\text{Zr},\text{Nb})_3\text{Fe}$, the extent to which this is the case is a subject for further work. To resolve the positions of the Zr, Nb and Fe in the hexagonal phase, Toffolon et al. used Rietveld refinement of XRD data on a hexagonal ternary phase of composition $\text{Zr}_{37.0}\text{Nb}_{26.5}\text{Fe}_{36.5}$ (at.%), which fits well with the $\text{Zr}(\text{Nb},\text{Fe})_2$ stoichiometric assignment [25]. Their work showed that the Nb and Fe are interchangeable on the $2a$ and $6h$ Wyckoff positions. It would be interesting to repeat this experiment for a hexagonal phase with a stoichiometry that fits well with the designation $(\text{Zr},\text{Nb})_3\text{Fe}$.

Table 1 The average compositions of the ternary ZrNbFe phases when designated as the hexagonal or cubic phase. Data taken from Figure 1.

Phase designation	Mean composition $\pm 1.96*\text{std}$ [at.%]				# Measurements
	Zr	Nb	Fe	Cr	
Hexagonal	35.6 ± 5.0	32.2 ± 14.4	30.8 ± 13.0	1.1 ± 5.4	112
Cubic	57.9 ± 10.9	10.1 ± 10.8	31.8 ± 5.2	-	43

Figure 8 An analysis of the variation in unit cell volume with changing phase composition for a) the hexagonal phase and b) the cubic phase. Data taken from Figure 1.

5.2.2 The cubic phase

The FCC $(\text{Zr,Nb})_2\text{Fe}$ phase dates back to the compositional range noted by Alekseeva and Korotkova in 1989 [55,56] but the alloy compositions studied at that time have since been reassessed and determined to consist of the two phases hexagonal and cubic designated $\text{Zr}(\text{Nb,Fe})_2$ and $(\text{Zr,Nb})_2\text{Fe}$ [21], as opposed to the originally-proposed single “T” phase. However, the name “T” phase has been retained by some Russian groups to describe the $(\text{Zr,Nb})_2\text{Fe}$ phase alone, which is present in higher volume fractions when the Fe:Nb ratio in the alloy is relatively high [3,22], for instance, in E635 with 0.65Fe (wt.%) as opposed to the usual 0.35Fe (wt.%) [27]. Due to the dependence of the cubic phase’s existence on the Fe:Nb ratio in the alloy, chemical heterogeneity in the as-cast material will also play a role in and this aspect of processing in relation to Zr-Nb-Fe intermetallic phases has not been investigated

to date. Therefore, triple melting is recommended for thorough mixing, especially for alloys in which long heat treatments are not possible. In the first instance of structure recognition, a cubic phase in ternary Zr-Nb-Fe systems was reported in 1999 by Mössbauer spectroscopy alone as a phase similar to Zr_2Fe but containing some Nb [63]. This was later confirmed by correlative analytical Mössbauer, X-ray diffraction and electron-based chemical quantification techniques [21,65] as $(\text{Zr,Nb})_2\text{Fe}$.

The identification of this cubic phase by electron microscopy techniques is somewhat easier than that of the hexagonal phase, as the amount of its constituents are so different to one another. This is demonstrated in Figure 1 and Figure 4 such that the number of atoms of $\text{Nb} < \text{Fe} < \text{Zr}$. In Table 1 we show the composition for this cubic phase as the mean $\pm 1.96*\text{std}$, which demonstrates the larger variability in the Zr and Nb content relative to

the Fe, reinforcing the stoichiometry $(\text{Zr,Nb})_2\text{Fe}$. In Figure 5b and Figure 5c we show the pairing of Nb with either the Fe or the Zr, respectively, to produce stoichiometries of approximately $(\text{Nb,Fe})_3\text{Zr}_4$ or $(\text{Zr,Nb})_2\text{Fe}$, respectively, only the latter of which has a binary equivalent and is therefore most likely. In comparison to the hexagonal phase in Figure 5a and Figure 5b, the stoichiometric assignment for this phase is much clearer. However, it was initially reported that the tetragonal Zr_2Fe has a lattice parameter approximately half that of FCC $(\text{Zr,Nb})_2\text{Fe}$ [63]. As such, the $(\text{Zr,Nb})_2\text{Fe}$ phase is sometimes referred to as $(\text{Zr,Nb})_4\text{Fe}_2$ to avoid any assumption that this FCC ternary phase holds any similarity to the tetragonal binary equivalent [3,22,25,66]. There is an FCC allotrope of Zr_2Fe with very similar lattice parameters to FCC $(\text{Zr,Nb})_2\text{Fe}$: $a = 1.221$ nm for FCC Zr_2Fe [57] and $a = 1.21$ - 1.23 nm for FCC $(\text{Zr,Nb})_2\text{Fe}$ [21,23,41,44]. Such similarity in lattice parameter may be expected if Nb is to replace some Zr at Zr lattice sites, which is reinforced by the different Fe environment observed in $(\text{Zr,Nb})_2\text{Fe}$ relative to Zr_2Fe [63]. However, due to the similarity in atomic mass of Zr and Nb, Rietveld refinement of powder X-ray diffraction spectra cannot distinguish between the two [25].

The trends in composition for the cubic phase are somewhat different to the hexagonal phase. In Figure 6d we show that there is a positive correlation between the cubic phase composition of Zr and the alloy Zr:Nb ratio, and, correspondingly, a negative correlation with Nb content in Figure 6e. Interestingly, the data from the cubic phase heat treated above and below the monotectoid do not follow on from one another as the data does for the hexagonal phase in Figure 6a-c). This demonstrates that there is a dependence of cubic phase composition on alloy composition but also that the effect of heat treatment temperature on the phase composition is more significant for the cubic phase than for the hexagonal phase. Although the result of this temperature effect is to retain compositional range for the variable Zr and Nb elements for both heat treatment regimes above and below the monotectoid, the lower temperature heat treatments do not do this as well and the 'fixed' Fe content is more

variable. This is easily explained from a thermodynamic equilibrium standpoint, suggesting that the organisation of atoms within the cubic phase is more well defined than those in the hexagonal. For alloys of similar Zr:Nb ratio but heat treated above or below the monotectoid, those below the monotectoid tend to have lower Zr content and higher Nb, which might be explained by Nb as a slow diffuser at lower temperatures. Above the monotectoid the Fe content is reasonably constant at 32-33 at.% but below the monotectoid the Fe content is quite variable at 25-37 at.%. We may conclude that the effect of heat treatment temperature is more severe for the cubic phase than for the hexagonal, but with the ambiguity in designation of hexagonal as $\text{Zr}(\text{Nb,Fe})_2$ or $(\text{Zr,Nb})_3\text{Fe}$ and will the latter of these being present predominantly below the monotectoid, it may be the case that the hexagonal is more prone to metastable phases below the monotectoid. The effect of changes in chemistry on unit cell volume for the cubic phase is assessed in Figure 8 for those studies that report both. In doing this, we observe little change in the composition with changing lattice parameter, especially in comparison to the hexagonal phase. The exact position of Zr and Nb in the lattice of the cubic phase therefore remains an open question, although it is likely valid that the Zr and Nb positions are interchangeable.

6 Irradiation Effects

It may be expected that secondary particles of the same phase will evolve under irradiation in a similar manner. Therefore, ambiguity in phase designation may be partly resolved by a study of the effects of irradiation on that phase. However, this prospect is complicated by a number of factors, namely variable phase composition, irradiation dose rate and irradiation temperature [68]. The following is an assessment of the irradiation response of the phases designated as hexagonal or cubic.

6.1 The hexagonal phase

The ternary phase commonly designated as hexagonal $\text{Zr}(\text{Nb,Fe})_2$ has been reported to display three different modes of behaviour under irradiation. The first mode is a uniform amorphisation at low temperature neutron

irradiations [27] (alloy E635, 60 °C, 6 dpa, $7.6 \times 10^{25} \text{ n m}^{-2}$, $2 \times 10^{18} \text{ n m}^{-2} \text{ s}^{-1}$, $1.6 \times 10^{-7} \text{ dpa s}^{-1}$) or under proton irradiation at a higher irradiation temperature and at a dose rate higher by two orders of magnitude [69] (alloy M5®, 350 °C, $2 \times 10^{-5} \text{ dpa s}^{-1}$). The second mode is partial amorphisation at the periphery of the particle, a “rare event” described in a single publication (alloy E635, 350 °C, 4 dpa, $5 \times 10^{25} \text{ n m}^{-2}$) [30]. The third and final mode reported is of no amorphisation whatsoever, but a loss of Fe and a transformation from the hexagonal structure to a BCC structure, which has been demonstrated in alloy E635 ($7 \times 10^{25} \text{ n m}^{-2}$, $3 \times 10^{17} \text{ n m}^{-2} \text{ s}^{-1}$) at temperatures of 315 °C [20], 330-350 °C [24,27] and in Low-Sn ZIRLO™ after BWR irradiation ($9 \times 10^{25} \text{ n m}^{-2}$, 18 dpa) at a temperature 280-330 °C [70]. Fe dissolution from the hexagonal secondary phase without amorphisation nor transformation has been observed under higher dose rate proton irradiation (2-7 dpa, $\sim 1 \times 10^{-7} \text{ dpa s}^{-1}$) at 350 °C [34]. Whilst most of these reports state that the initial composition of the ternary phases most closely resembled $\text{Zr}(\text{Nb,Fe})_2$, even though there is no detailed characterisation, there has been a report of a better fit for the initial composition of the ternary phase as $(\text{Zr,Nb})_3\text{Fe}$ in alloy Zr-2.5Nb, with post-irradiation analysis demonstrating uniform depletion of Fe and a transformation within the whole particle from a monocrystalline state to a polycrystalline state ($1.6 \times 10^{25} \text{ n m}^{-2}$, $\sim 2.6 \text{ dpa}$, 250-300 °C) [71].

There are three well-defined irradiation temperature regimes for the $\text{Zr}(\text{Fe,Cr})_2$ Laves phase in the Zircaloys. The first is a uniform amorphisation at low temperature neutron irradiation [72] and under irradiation with ions at higher temperatures [73,74]. The second regime is at normal operating irradiation temperatures and results in Fe loss and coupled amorphisation progressing from the particle periphery inwards with increasing irradiation dose [72,73,75,76], this process being quicker at the lower end of the operating temperature range at 270 °C [77]. The final regime is at high neutron or proton irradiation temperatures and results in Fe loss without amorphisation, re-precipitation in the matrix and even particle growth

[53,67,75,78]. Whilst these temperature regimes may show resemblance to the three modes of evolution in the hexagonal ZrNbFe phase, it is important to note that, for the Zr-Nb-Fe alloys, the particle(s) that display progressive amorphisation and those that display transformation from HCP to BCC were irradiated in the same temperature and dose rate regime, yet they were reported to be the same phase initially. Such a difference in behaviour for the same phase could only be due to either a significantly wide variation in initial phase composition, which was not detailed in that publication, or, alternatively, a different initial phase entirely. A lack of statistically relevant and quantitative characterisation of particles in the initial condition and the ambiguity in designation of the hexagonal phase between $\text{Zr}(\text{Nb,Fe})_2$ and $(\text{Zr,Nb})_3\text{Fe}$ (see section 5) compounds this problem.

The characterisation of particles in the three temperature regimes is much better documented in the Zircaloys than in the ZrNbFe alloys. Mechanistic explanations for differing behaviour as a function of temperature have their foundation in the competition between irradiation damage rate and thermal annealing of that damage with regards to the homologous temperature for a particular phase, its stoichiometric range and its capability for self-solubility in the defective state [53,67,79,80]. However, there is a significant difference in the behaviour of the Zircaloy $\text{Zr}(\text{Fe,Cr})_2$ and the hexagonal phase in ZrNbFe alloys; the latter undergoes a structural transformation and the former does not. This may be explained by a greater diffusion coefficient in $\alpha\text{-Zr}$ for Cr relative to Nb [81] and the β -stabilising nature of Nb in Zr, but more work is required to assess the self-solubility and stoichiometric range of the ZrNbFe secondary phases in both their initial and defective states.

There is an inherent difficulty in post-mortem analyses of phases; after irradiation there is commonly Fe depletion from Fe-containing precipitates and so the initial phase composition and therefore phase designation becomes difficult, especially when there are conflicting or incomplete reports of phase composition prior to irradiation, i.e.

Zr(Nb,Fe)₂ or (Zr,Nb)₃Fe. Accurate, spatially resolved chemical data on a statistical number of particles should therefore be an essential part of any systematic study, and developments in in situ heavy ion TEM studies will allow a direct assessment of individual particles' evolution during irradiation.

6.2 The cubic phase

Under neutron irradiation the cubic phase (Zr,Nb)₂Fe retains its crystalline core and shows a polycrystallinity at the particle periphery that is likely Nb-rich platelets [14,43]. Whilst EDS line-scans have been used to demonstrate Fe-depletion from only the particle periphery coincident with the Nb platelet precipitation [14], such trends can be attributed to particle edge effects. Particle extraction alleviates this issue and Kobylansky et al. have demonstrated a decrease in average Fe content in the cubic phase from an initial 29 at.% to 23.5 at.% in alloy NSF and 25.2 at.% in alloy E635, coincident with increases in Zr and Nb content [43]. As these particles were extracted from the matrix, this decrease in Fe content cannot be attributed to the precipitation of Nb-rich phases. The irradiation-induced polycrystallinity is reminiscent of a similar phenomenon observed by Griffiths et al. in a particle designated (Zr,Nb)₃Fe in alloy Zr-2.5Nb (wt.%) [71], which, in similarity to the post-irradiation composition of the cubic phase initially (Zr,Nb)₂Fe, also has an Fe content of 25 at.%. The decrease in Fe content in (Zr,Nb)₂Fe and any recrystallization to polycrystallinity may indicate a range of metastable states after low temperature heat treatments. This idea is supported by the larger variability in phase composition at temperatures below the monotectoid temperature, < 600 °C, in Figure 6f of this review.

7 Conclusions

The presence of Fe in β -Nb phase seems only to be convincing in alloys that are either quenched from temperatures above the monotectoid for β -Zr decomposition or in model alloys in which the Fe content is high. In other cases, it seems that Fe is contained at the interfacial region between α -Zr and β -Nb. This highlights the importance of spatially

resolved chemical analysis and/or phase extraction techniques in preparation for the study of individual phases, independent from any matrix in which they may be embedded. Any excess of Fe is therefore likely to be found in interfacial regions or in a low volume fraction of ternary Zr-Nb-Fe phases.

The ternary phase cubic (Zr,Nb)₂Fe is reasonably well defined due to its strict adherence to stoichiometry, especially at temperatures above the monotectoid. However, approximately one third of compositions reported as hexagonal Zr(Nb,Fe)₂ fit well with the stoichiometry (Zr,Nb)₃Fe in analogy to the binary equivalent Zr₃Fe, and from the early 1990s to the year 2000 this alternative stoichiometry was reported in a few publications as having the same structure as Zr(Nb,Fe)₂. It is therefore either the case that Zr(Nb,Fe)₂ has an extraordinarily wide stoichiometric range, which would be unusual for a Laves phase, or that there are metastable phases that form as a result of the slow diffusion of Nb during heat treatments below the monotectoid for β -Zr decomposition, or that the errors in the analyses are inordinately large. A detailed body of work is required that concerns commercial-type alloys and the phases that are present above and below the ZrNb monotectoid, with correlative quantitative chemical and structural analyses to assess composition, crystallography and, ideally, local Fe environments with parallel Mössbauer and modelling approaches.

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