

# Liquidus Projection Surface and Isothermal Section at 1200 °C of Ni-Ru-Y

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Scanning electron microscopy studies with energy dispersive x-ray analyses of as-cast and annealed samples of Ni-Ru-Y were used to produce a solidification projection, a liquidus projection surface and an isothermal section at 1200 °C. The  $\sim\text{YNi}_2$ ,  $\sim\text{YNi}_3$  and  $\sim\text{YRu}_2$  phases had wider solubilities than line compounds, and also extended the furthest into the system. The binary phase extensions into the ternary were:  $\sim 51$  at.% Ru for  $\sim\text{YNi}_2$ ;  $\sim 22$  at.% Ru for  $\sim\text{YNi}_3$ ;  $\sim 13$  at.% Ru for  $\sim\text{YNi}_5$ ;  $\sim 7$  at.% Ru for  $\sim\text{YNi}$ ;  $\sim 12$  at.% Ni for  $\sim\text{YRu}_2$  and  $\sim 10$  at.% for  $\sim\text{Y}_{44}\text{Ru}_{25}$ . Ruthenium stabilised  $\sim\text{YNi}_2$ , so that it solidified at a higher temperature in the ternary than in the Ni-Y binary. A ternary phase was confirmed at  $\text{Y}_{51}\text{Ru}_{15}\text{Ni}_{34}$  (at.%), which forms in a peritectic reaction. The  $\sim\text{Y}_3\text{Ru}$  and  $\sim\text{Y}_3\text{Ni}$  phases were isomorphous and formed a continuous solid solution. Heat treatment at 1200 °C gave the phases: (Ru),  $\sim\text{YRu}_2$ ,  $\sim\text{YNi}_2$ ,  $\sim\text{YNi}_3$ ,  $\sim\text{YNi}_4$ ,  $\sim\text{YNi}_5$  and (Y).

**Keywords** scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), isothermal section 1200 °C, liquidus surface projection, Ni-Ru-Y, ternary phase diagram

## 1. Introduction

The Ni-Ru-Y system was studied for a potential new coating material. It is of interest because ruthenium increases the corrosion resistance of titanium alloys,<sup>[1]</sup> hardmetals<sup>[2]</sup> and stainless steels,<sup>[3]</sup> and yttrium has been used as a component for coating Ni-based alloys.<sup>[4]</sup>

The Ni-Ru (Fig. 1) and Ni-Y (Fig. 2) binary phase diagrams are well established, but the reactions in Ru-Y are less certain, although the phases are known (Fig. 3).<sup>[5]</sup> The Ni-Y and Ru-Y phase diagrams are complex with many

phases,<sup>[5]</sup> whereas Ni-Ru is a simple peritectic, with no intermetallic phases.

A structure type for  $\text{Y}(\text{Ru}_x\text{Ni}_{1-x})_2$ , where  $x = 0 - 0.78$  (i.e.  $\sim\text{YNi}_2$  up to  $\text{Y}_{33}\text{Ru}_{52}\text{Ni}_{15}$ ) was reported as  $\text{Cu}_2\text{Mg}$ .<sup>[6]</sup> Chunxiao et al.<sup>[7]</sup> studied the transect from  $\text{YNi}_2$  to  $\text{YRu}_2$  in Ni-Ru-Y and found a two-phase region between the binary phase extensions, and that  $\sim\text{YNi}_2$  extended much further into the ternary than  $\sim\text{YRu}_2$ . Both  $\text{YNi}_2$  and  $\text{YRu}_2$  are Laves phases;  $\text{YNi}_2$  has the  $\text{Cu}_2\text{Mg}$  structure, and  $\text{YRu}_2$  has the  $\text{Zn}_2\text{Mg}$  structure.<sup>[8]</sup>

Sokolovskaya et al.<sup>[9]</sup> produced an isothermal section at 600 °C for Ni-Ru-Y. For the terminal solid solutions, (Ni) was shown with solubility for only ruthenium, and (Ru) was shown with considerable solubility for nickel. In the redrawn version (Fig. 4),<sup>[10,11]</sup> (Ru) was drawn with less solubility for Ni, but both solubilities decrease with temperature,<sup>[5]</sup> and phases which had previously been drawn as line compounds,<sup>[9]</sup> were drawn with small solubility ranges. Not all of the accepted binary intermetallic phases<sup>[5]</sup> were indicated on the isothermal section, and the missing phases were:  $\text{Y}_2\text{Ni}_7$ ,  $\text{Y}_3\text{Ni}_2$ ,  $\text{Y}_3\text{Ru}_2$ ,  $\text{Y}_{44}\text{Ru}_{25}$  and  $\text{Y}_5\text{Ru}_2$ . The reason for this is probably that the phases did not penetrate the ternary sufficiently for the samples to contain them, and the original paper<sup>[9]</sup> did not provide sample compositions. There was no solubility shown in Y. All the binary phases present were shown to extend into the ternary as line compounds, along constant Y content.<sup>[9]</sup> At 600 °C, the extent of  $\sim\text{Y}_3\text{Ni}$  was at  $\sim\text{Y}_{75}:\text{Ru}_6:\text{Ni}_{19}$  (at.%) and the extent of  $\sim\text{Y}_3\text{Ru}$  was at  $\text{Y}_{75}:\text{Ru}_{17}:\text{Ni}_8$  (at.%). The phase extents of  $\sim\text{YNi}_2$  and  $\sim\text{YRu}_2$  agreed well with Chugxiao et al.<sup>[7]</sup> and these phases extended towards each other, with a two-phase region between. It should be noted that, considering the tie-triangles (three-phase regions) and the two-phase regions, there are no true ternary phases on that transect, and the extents of the  $\text{YNi}_2$  and  $\text{YRu}_2$  phases are  $\sim\text{Y}_{34}:\text{Ru}_{49}:\text{Ni}_{17}$  and  $\sim\text{Y}_{34}:\text{Ru}_{55}:\text{Ni}_{11}$  (at.%) respectively. These phase extension limits are marked on the most

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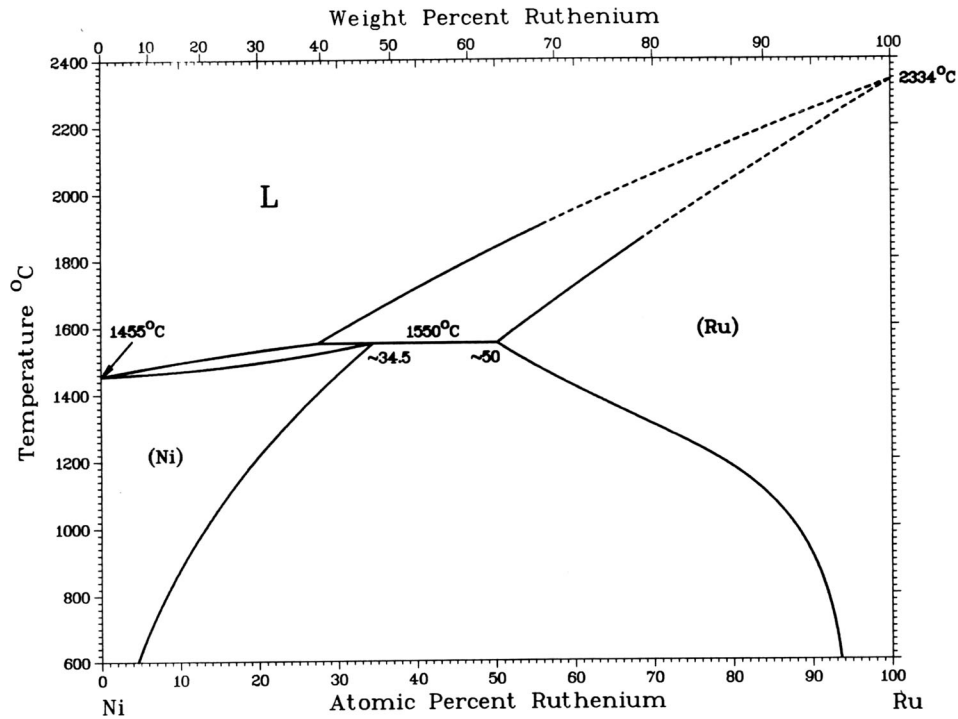


Fig. 1 Ni-Ru phase diagram<sup>[5]</sup>

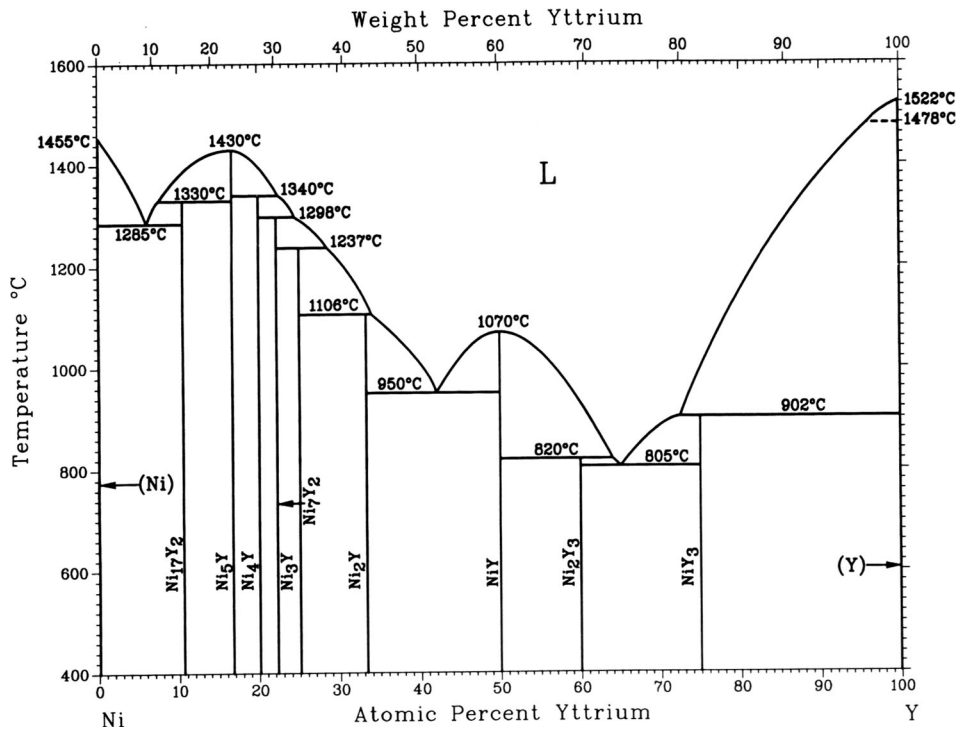


Fig. 2 Ni-Y phase diagram<sup>[5]</sup>

recent compilation diagrams.<sup>[10,11]</sup> The phase widths were drawn to be  $\sim 1$  at.% in the compilation (Fig. 4),<sup>[11,12]</sup> wider than in the original.<sup>[9]</sup> A true ternary phase,  $\sim Y_5Ru_2Ni_2$ ,<sup>[9]</sup> was reported with a solubility range of  $\sim 5$  at.%, which was

involved in four three-phase fields,<sup>[9]</sup> but in the subsequent compilations,<sup>[10,11]</sup> the range was smaller. In this investigation, the ternary phase is denoted  $\tau$ , or  $\sim Y_{51}Ru_{15}Ni_{34}$  (at.%).

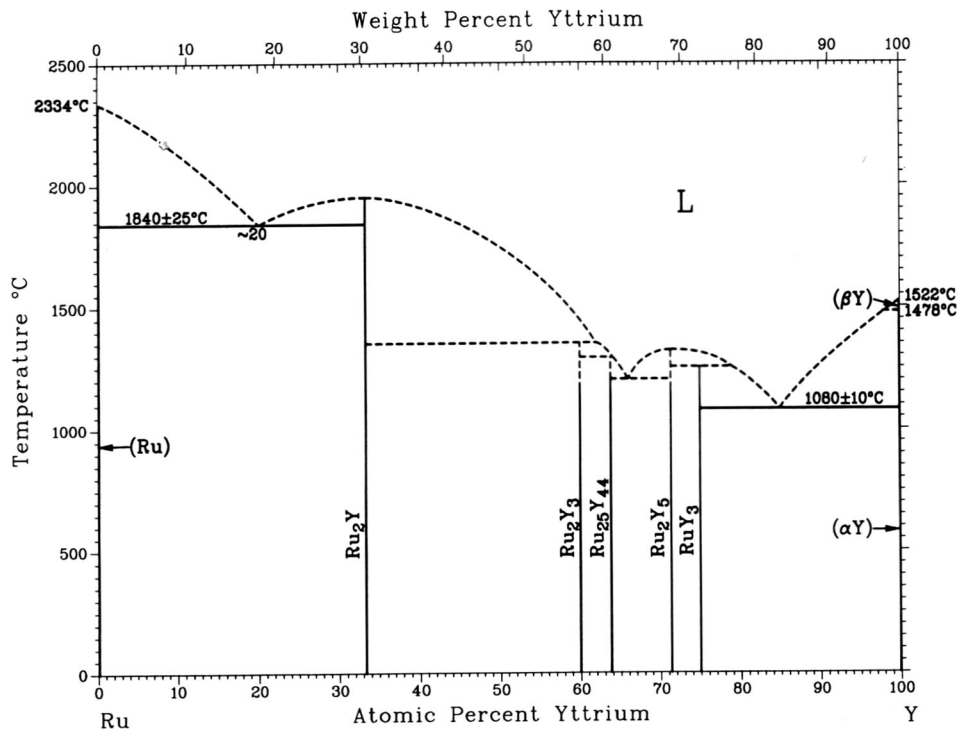


Fig. 3 Ru-Y phase diagram<sup>[5]</sup>

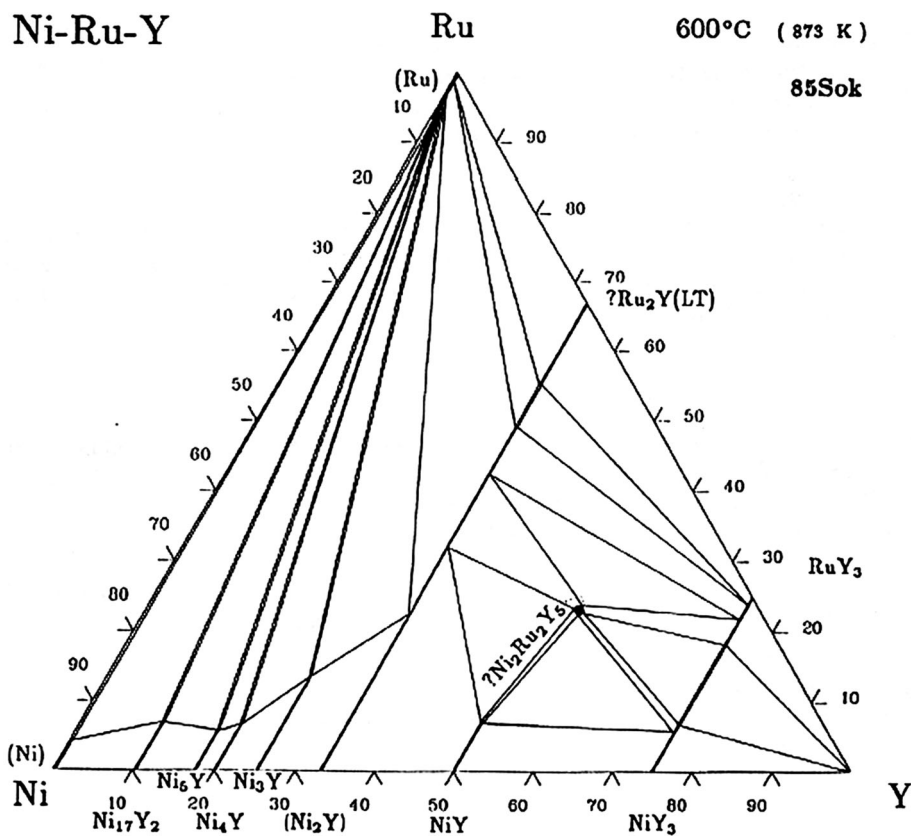


Fig. 4 Isothermal section of Ni-Ru-Y (at.%) at 600 °C<sup>[10,11]</sup>, redrawn from Sokolovskaya et al<sup>[9]</sup>

**Table 1 Starting elements**

Element	Purity	Condition	Impurities, ppm	Supplier
Ni	99.99+%	Powder 150 µm max	Ag 1, Al 1, Ca 1, Cr < 1, Cu 3, Fe 15, Mg < 1, Mn < 1, Si 2, Sn < 1	1
Ru	99.9%	Lump	Unknown	2
Y	99.9%	Lump	Al 10, Ca 30, Cu 10, Dy 2, Er 2, Eu 12, Fe 15, Gd 30, Mg 5, Si 10, Ta 300, Tm 1, Yb 5	1

1 Purchased from Goodfellow Cambridge Ltd., Huntingdon, England

2 From the Platinum Development Initiative (PDI) (Anglo Platinum, Lonmin and Impala) through Mintek, South Africa

The aim of this work was to study as-cast alloys, and derive a liquidus surface. Additionally, samples were annealed at 1200 °C, and compared to the lower temperature results of the isothermal section at 600 °C.<sup>[9,10]</sup> The phase nomenclature is given in Pettifor order.<sup>[12]</sup> Although some preliminary work has already been published from the current study,<sup>[13-19]</sup> this is the final version, and some of the interpretations have been changed using evidence from more samples.

## 2. Experimental Procedure

The samples were made by arc-melting minimum 99.9% pure elemental components, Table 1, under an argon atmosphere, after pumping out and flushing repeatedly with argon, and titanium was used as an oxygen-getter. The samples were then sectioned, as near as possible into halves, mounted, and prepared metallographically. The first five samples were also sealed in silica ampoules, back-filled with argon, and annealed at 1200 °C (rather than the planned 1000 °C) for 1000 h. Although there was a concern that Y could reduce SiO<sub>2</sub>, there were no other methods available.

Analyses were undertaken using pure element standards, in a Philips XL 30 ESEM with an EDAX Phoenix EDX system, and at least five analyses were taken on different phases or over areas to obtain the averages presented. The phases were identified by comparing the compositions to the 600 °C isothermal section,<sup>[9]</sup> the binaries<sup>[5]</sup> and also using the phase morphologies in the microstructures. When not in use, the samples were stored in ethanol or methanol. Unfortunately, most of the samples oxidized and disintegrated before x-ray diffraction (XRD) could be undertaken to confirm the phases, but some were analysed on a Philips PW 3710 powder diffractometer giving patterns of poor quality.

## 3. Results

Some of the alloys had small particles of Y<sub>2</sub>O<sub>3</sub>, which were assumed to be present before, or in an early stage of melting, despite taking the precautions of melting under argon and storing in alcohol. Since the oxide particles were mainly in minor proportions, and have a very high melting point (2458 °C),<sup>[5]</sup> they were ignored in the interpretation of the microstructures, despite the fact that they were some-

times nucleation sites. Although these particles were analysed, being more brittle, they were usually at least partially removed on sample preparation and the resulting poor surface gave low wt% totals and high errors. Ignoring the oxides in the samples' compositions, the solidification sequences were justified since attempts to interpret them as (Y), which then subsequently oxidized, gave impossible solidification reaction sequences for most of the samples, except for the very Y-rich samples. However, regions with Y<sub>2</sub>O<sub>3</sub> were avoided as far as possible during analysis. Another problem was that all the high Y content samples were found to be contaminated with Ta. Subsequently, when the pure Y source material was studied, 1-1.5 µm diameter Ta-rich spheroids were found. Since in energy dispersive x-ray analysis (EDX), the Ni K<sub>α</sub> peak overlaps the Ta L<sub>α</sub> peak, and the Y L<sub>α</sub> peak overlaps with the Ta M<sub>α</sub> peak, this made deconvoluting the presence of Ta very difficult, although Ta regions were always very bright in the microstructure in backscattered electron imaging mode (BSE), with Ta (73) having a much higher atomic number than Ni (28), Y (39) or Ru (44).

The EDX analyses for the overall composition of the alloys and the composition of the individual phases of the as-cast samples are given in Table 2, with all compositions in at.%, while the area analyses of the eutectic structures are listed in Table 3. The analyses for the heat treated samples at 1200 °C for 1000 h are given in Table 4.

Unfortunately, the specimens oxidized and disintegrated very soon after scanning electron microscopy (SEM) analysis, and thus most of the samples were not suitable for XRD studies. Even keeping some of the samples in analar grade (AR) methanol and some of the samples in ultra low water (UL) ethanol did not protect the samples. An original sample of composition ~Ni<sub>15</sub>:Ru<sub>15</sub>:Y<sub>70</sub> (at.%), i.e. high Y content, oxidized almost immediately and was never examined, and Sample 2, ~Ni<sub>54</sub>:Ru<sub>45</sub>:Y<sub>1</sub> (at.%), although Y-poor, disintegrated soon after analysis. It was subsequently found that water readily reacts with Y and its compounds to form hydrogen and Y<sub>2</sub>O<sub>3</sub>,<sup>[20]</sup> and this is likely to have occurred during metallographic preparation.

### 3.1 As-Cast Samples

**3.1.1 Nominal ≈Ni<sub>7</sub>:Ru<sub>72</sub>:Y<sub>21</sub> (at.%), Sample 12.** The nominal composition ~Ni<sub>7</sub>:Ru<sub>72</sub>:Y<sub>21</sub> (at.%), Sample 12, solidified with (Ru) dendrites in a complex eutectic matrix (Fig. 5). The darkest phase showed a wide range of coring, and formed after the fine univariant binary (Ru) + ~YRu<sub>2</sub> eutectic.

**Table 2 Overall compositions of the alloys and phase analyses of the as-cast Ni-Ru-Y alloys (at.%), with values in ranges obtained from cored phases, and the error is associated with both values**

Sample no.	Y: Ru:Ni	Overall analysis		(Ru) Y: Ru:Ni	$\sim YRu_2$ Y: Ru:Ni	$\sim YNi_2$ Y: Ru:Ni	(Ni) Y: Ru:Ni	$\sim Y_2Ni_{17}$ Y: Ru:Ni	$\sim YNi_5$ Y: Ru:Ni	$\sim YNi_3$ Y: Ru:Ni	$\sim YNi_4$ Y: Ru:Ni	$\sim Y_{44}Ru_{25}$ Y: Ru:Ni	$\tau$	$\sim YNi$ Y: Ru:Ni	$\sim Y_3Ni_2$ Y: Ru:Ni	$\sim Y_3(Ru,Ni)$ Y: Ru:Ni	$\sim (Y) Y: Ru:Ni$
		(Ru) Y: Ru:Ni	Y: Ru:Ni														
12	20.7 ± 0.2	0.6 ± 1.2	31.6 ± 0.5	29.5 ± 2.7	...	...	...	...	...	...	...	...	...	...	...	...	...
	72.0 ± 0.8	97.8 ± 0.5	64.6 ± 0.7	50.7 ± 7.0	...	...	...	...	...	...	...	...	...	...	...	...	...
	7.3 ± 0.1	1.6 ± 0.4	3.8 ± 0.6	19.8 ± 8.8	...	...	...	...	...	...	...	...	...	...	...	...	...
2	1.0 ± 0.2	0.8 ± 0.4	...	...	0.3 ± 0.1	...	...	10.0 ± 1.5	...	...	...	...	...	...	...	...	...
	44.8 ± 0.7	55.0 ± 2.6	...	...	29.3 ± 0.3	...	...	11.4 ± 2.1	...	...	...	...	...	...	...	...	...
	54.2 ± 0.7	44.2 ± 0.3	...	...	70.4 ± 0.3	...	...	78.6 ± 0.6	...	...	...	...	...	...	...	...	...
6	19.7 ± 0.2	0.9 ± 0.1	...	23.7 ± 0.3	...	...	...	...	20.8 ± 0.2	Too small	...	...	...	...	...	...	...
	41.7 ± 0.3	89.0 ± 1.0	...	46.1 ± 0.6	...	...	...	...	22.1 ± 0.6	...	...	...	...	...	...	...	...
	38.6 ± 0.5	10.1 ± 1.0	...	30.2 ± 0.7	...	...	...	...	57.1 ± 0.6	...	...	...	...	...	...	...	...
5	14.7 ± 0.2	1.7 ± 0.5	...	...	...	...	...	15.6 ± 0.2	...	...	...	...	...	...	...	...	...
	16.3 ± 0.2	71.2 ± 2.0	...	...	...	...	...	13.1 ± 0.4	...	...	...	...	...	...	...	...	...
	69.0 ± 0.2	27.1 ± 1.6	...	...	...	...	...	71.3 ± 0.3	...	...	...	...	...	...	...	...	...
13	11.3 ± 0.3	...	...	...	...	Too small	...	14.7 to 11.8 ± 2.5	...	...	...	...	...	...	...	...	...
	12.9 ± 0.2	...	...	...	...	...	...	11.7 to 12.6 ± 2.2	...	...	...	...	...	...	...	...	...
	75.8 ± 0.3	...	...	...	...	...	...	73.6 to 75.6 ± 2.5	...	...	...	...	...	...	...	...	...
7	8.6 ± 0.1	...	...	...	...	Too small	...	10.5 ± 0.2	...	...	...	...	...	...	...	...	...
	10.3 ± 0.1	...	...	...	...	...	...	8.6 ± 0.3	...	...	...	...	...	...	...	...	...
	81.1 ± 0.2	...	...	...	...	...	...	80.9 ± 0.2	...	...	...	...	...	...	...	...	...
8	28.8 ± 0.6	...	...	29.3 ± 2.5	...	...	...	...	23.7 ± 0.1	...	...	...	...	...	...	...	...
	10.1 ± 0.1	...	...	14.4 ± 2.2	...	...	...	...	5.5 ± 0.8	...	...	...	...	...	...	...	...
	61.1 ± 0.6	...	...	56.3 ± 1.9	...	...	...	...	70.8 ± 0.8	...	...	...	...	...	...	...	...
16	26.6 ± 0.1	...	...	30.7 ± 3.0	...	...	21.2 ± 2.8	...	26.8 ± 0.1	20.1 ± 0.2	...	...	...	...	...	...	...
	3.1 ± 0.1	...	...	3.1 ± 0.1	...	...	3.4 ± 0.7	...	3.9 ± 0.3	2.7 ± 0.1	...	...	...	...	...	...	...
	70.3 ± 1.5	...	...	66.2 ± 2.3	...	...	75.4 ± 2.9	...	69.3 ± 0.5	77.2 ± 0.2	...	...	...	...	...	...	...
3	35.3 ± 0.1	...	32.4 ± 0.3	32.5 ± 0.1	...	...	...	...	...	...	...	...	Eut.	...	...	...	...
	45.3 ± 0.3	...	55.4 ± 2.0	43.7 ± 3.3	...	...	...	...	...	...	...	...	...	...	...	...	...
	19.4 ± 0.4	...	12.2 ± 1.9	23.8 ± 3.2	...	...	...	...	...	...	...	...	...	...	...	...	...
11	58.8 ± 0.2	...	...	34.8 ± 5.5	...	...	...	...	...	...	...	...	Eut.	...	...	...	...
	31.1 ± 0.2	...	...	49.8 ± 4.3	...	...	...	...	...	...	...	...	...	61.4 ± 0.2	...	...	...
	10.1 ± 0.3	...	...	15.4 ± 1.2	...	...	...	...	...	...	...	...	...	32.1 ± 1.0	...	...	...
17	62.7 ± 0.2	...	...	34.7 ± 0.1	...	...	...	...	...	...	...	...	Eut.	...	...	...	...
	31.3 ± 0.5	...	...	49.3 ± 1.9	...	...	...	...	...	...	...	...	...	33.0 ± 0.3	...	...	...
	6.0 ± 0.3	...	...	16.0 ± 1.8	...	...	...	...	...	...	...	...	...	3.8 ± 0.3	...	...	...
18	60.8 ± 0.2	...	...	35.6 ± 0.1	...	...	...	...	...	...	...	...	...	64.7 ± 0.2	55.0 ± 0.3	...	...
	22.6 ± 0.1	...	...	48.7 ± 0.4	...	...	...	...	...	...	...	...	...	25.4 ± 0.2	13.9 ± 0.4	...	...
	16.6 ± 0.3	...	...	15.7 ± 0.4	...	...	...	...	...	...	...	...	...	9.9 ± 0.6	31.1 ± 0.7	...	...
1	50.0 ± 0.1	...	...	32.9 ± 0.1	...	...	...	...	...	...	...	...	...	Eut.	Eut.	...	...
	25.6 ± 0.1	...	...	48.3 ± 1.2	...	...	...	...	...	...	...	...	...	...	...	...	...
	24.4 ± 0.1	...	...	18.8 ± 1.2	...	...	...	...	...	...	...	...	...	...	...	...	...

**Table 2 continued**

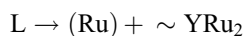
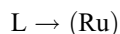
Sample no.	Overall analysis	Y: Ru:Ni	(Ru) Y: Ru:Ni	$\sim YRu_2$ Y: Ru:Ni	$\sim YNi_2$ Y: Ru:Ni	(Ni) Y: Ru:Ni	$\sim Y_2Ni_{17}$ Y: Ru:Ni	$\sim YNi_5$ Y: Ru:Ni	$\sim YNi_3$ Y: Ru:Ni	$\sim YNi_4$ Y: Ru:Ni	$\sim Y_{44}Ru_{25}$ Y: Ru:Ni	$\tau$	$\sim YNi$ Y: Ru:Ni	$\sim Y_3Ni_2$ Y: Ru:Ni	$\sim Y_3(Ru,Ni)$ Y: Ru:Ni	$\sim (Y) Y: Ru:Ni$
4	43.1±0.3	...	...	31.1±0.1	...	...	...	...	...	...	...	I. den.	47.3±0.6	...	...	...
	15.6±0.2	...	...	35.7±0.8	...	...	...	...	...	...	...		6.3±0.9	...	...	...
	41.3±0.2	...	...	33.2±0.9	...	...	...	...	...	...	...		46.4±1.0	...	...	...
9	58.6±0.2	...	...	...	...	...	...	...	...	...	...	59.5±0.2	53.5±0.2	...	...	...
	10.7±0.2	...	...	...	...	...	...	...	...	...	...	13.8±0.5	6.6±2.9	...	...	...
	30.7±0.2	...	...	...	...	...	...	...	...	...	...	26.7±0.4	39.9±6.4	...	...	...
19	65.8±0.4	...	...	...	...	...	...	...	...	...	...	67.6±1.2	58.2±2.2	...	...	...
	7.7±0.4	...	...	...	...	...	...	...	...	...	...	10.7±1.5	2.6±0.9	...	...	...
	26.5±0.6	...	...	...	...	...	...	...	...	...	...	21.7±2.5	39.2±3.1	...	...	...
14	78.1±0.2	...	...	...	...	...	...	...	...	...	...	...	...	77.6 to 78.5±0.5	...	...
	12.1±0.3	...	...	...	...	...	...	...	...	...	...	...	...	14.8-7.9±0.7	...	...
	9.8±0.4	...	...	...	...	...	...	...	...	...	...	...	...	7.6-13.6±0.8	...	...
10	78.3±0.2	...	...	...	...	...	...	...	...	...	...	...	...	76.1±0.4	...	89.8±6.1
	11.2±0.4	...	...	...	...	...	...	...	...	...	...	...	...	13.3±0.6	...	3.8±3.1
	10.5±0.6	...	...	...	...	...	...	...	...	...	...	...	...	10.6±0.6	...	6.4±3.1
15	83.6±0.3	...	...	...	...	...	...	...	...	...	...	...	...	79.7±0.4	...	83.0±0.4
	6.1±0.3	...	...	...	...	...	...	...	...	...	...	...	...	12.8±0.9	...	10.5±0.3
	10.3±0.3	...	...	...	...	...	...	...	...	...	...	...	...	7.5±1.1	...	6.5±0.3

Eut. = eutectic component; I. den. = inner dendrite; and Too small = too small to analyse.  $\tau = Y_{51}Ru_{15}Ni_{34}$  (at.%)

**Table 3 Overall compositions of the univariant binary eutectics in the as-cast Ni-Ru-Y alloys (at.%); sparse eutectic in Sample 4 was not analysed**

Sample No.	Overall sample analysis Y: Ru:Ni	Area eutectic analysis			Eutectic components
		Y	Ru	Ni	
12	20.7 ± 0.2 72.0 ± 0.8 7.3 ± 0.1	18.8 ± 1.4	76.1 ± 1.0	5.1 ± 1.0	(Ru) + ~YRu <sub>2</sub>
2	1.0 ± 0.2 44.8 ± 0.7 54.2 ± 0.7	8.7 ± 0.4	12.2 ± 0.7	79.1 ± 0.6	(Ni) + ~YNi <sub>5</sub>
5	14.7 ± 0.2 16.3 ± 0.2 69.0 ± 0.2	12.5 ± 0.2	22.0 ± 0.4	65.5 ± 0.4	(Ru) + ~YNi <sub>5</sub>
13	11.3 ± 0.3 12.9 ± 0.2 75.8 ± 0.3	9.3 ± 0.2	14.8 ± 0.5	75.9 ± 0.6	(Ni) + ~YNi <sub>5</sub>
7	8.6 ± 0.1 10.3 ± 0.1 81.1 ± 0.2	6.8 ± 0.3	12.1 ± 0.2	81.1 ± 0.3	(Ni) + ~YNi <sub>5</sub>
3	35.3 ± 0.1 45.3 ± 0.3 19.4 ± 0.4	50.7 ± 2.8	14.9 ± 4.3	34.4 ± 7.0	~YNi <sub>2</sub> + τ, Y <sub>51</sub> Ru <sub>15</sub> Ni <sub>34</sub>
11	58.8 ± 0.2 31.1 ± 0.2 10.1 ± 0.3	55.2 ± 0.2	20.2 ± 0.3	24.6 ± 0.3	~Y <sub>44</sub> Ru <sub>25</sub> + τ, Y <sub>51</sub> Ru <sub>15</sub> Ni <sub>34</sub>
17	62.7 ± 0.2 31.3 ± 0.5 6.0 ± 0.3	57.0 ± 1.4	19.3 ± 1.1	23.7 ± 2.2	~Y <sub>44</sub> Ru <sub>25</sub> + τ, Y <sub>51</sub> Ru <sub>15</sub> Ni <sub>34</sub>
18	60.8 ± 0.2 22.6 ± 0.1 16.6 ± 0.3	58.6 ± 0.5	18.3 ± 0.4	23.1 ± 0.7	~Y <sub>44</sub> Ru <sub>25</sub> + τ, Y <sub>51</sub> Ru <sub>15</sub> Ni <sub>34</sub>
1	50.0 ± 0.1 25.6 ± 0.1 24.4 ± 0.1	54.6 ± 0.2	18.6 ± 1.7	26.8 ± 0.3	~Y <sub>44</sub> Ru <sub>25</sub> + τ, Y <sub>51</sub> Ru <sub>15</sub> Ni <sub>34</sub>
10	78.3 ± 0.2 11.2 ± 0.4 10.5 ± 0.6	81.9 ± 1.0	8.7 ± 0.8	9.4 ± 0.3	~Y <sub>3</sub> (Ru,Ni) + (Y)
15	83.6 ± 0.3 6.1 ± 0.3 10.3 ± 0.3	79.0 ± 0.7	12.4 ± 0.5	8.6 ± 0.3	~Y <sub>3</sub> (Ru,Ni) + (Y)

The solidification reactions were:

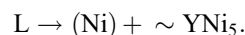
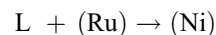
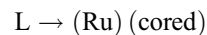


where the latter was a ternary peritectic reaction.

**3.1.2 Nominal  $\approx \text{Ni}_{54}:\text{Ru}_{45}:\text{Y}_1$  (at.%), Sample 2.** The nominal  $\sim \text{Ni}_{54}:\text{Ru}_{45}:\text{Y}_1$  (at.%) sample solidified with very cored (Ru) dendrites, followed by very clear peritectially-formed (Ni) (Fig. 6). There were very small areas of a globular (Ni) +  $\sim \text{YNi}_5$  eutectic. These were much too fine

to analyse the components accurately (and even the overall composition of the eutectic were just on the limit for reasonable analyses).

The solidification sequence was:

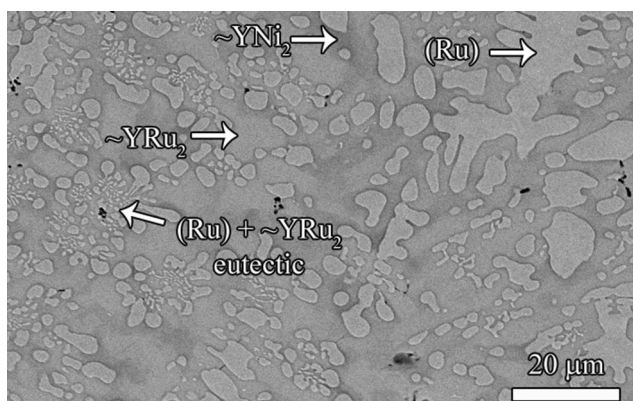


**3.1.3 Nominal  $\text{Ni}_{38}:\text{Ru}_{42}:\text{Y}_{20}$  (at.%), Sample 6.** The  $\text{Ni}_{38}:\text{Ru}_{42}:\text{Y}_{20}$  (at.%) sample (Sample 6) had small primary (Ru) dendrites (Fig. 7). Next in the solidification sequence

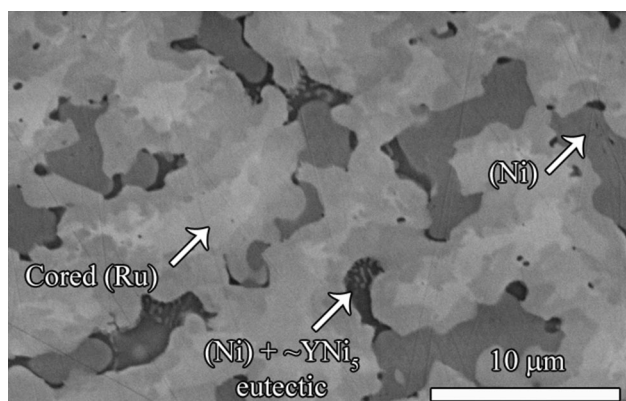


**Table 4 Overall compositions of the alloys and phase analyses of the Ni-Ru-Y alloys annealed at 1200 °C (at.%); samples with different regions are given increasing numbers working inwards**

Sample No.	Overall analysis Y: Ru:Ni	(Ru) Y: Ru:Ni	$\sim YRu_2$ Y: Ru:Ni	$\sim YNi_2$ Y: Ru:Ni	$\sim YNi_5$ Y: Ru:Ni	$\sim YNi_3$ Y: Ru:Ni	$\sim YNi_4$ Y: Ru:Ni
6H-1	12.4 ± 0.4	0.6 ± 0.1	...	...	16.0 ± 0.1	...	...
	24.8 ± 1.1	92.1 ± 0.7	...	...	8.0 ± 0.1	...	...
	62.8 ± 0.9	7.3 ± 0.7	...	...	76.0 ± 0.2	...	...
6H-2	16.1 ± 0.6	0.7 ± 0.2	...	...	...	...	21.5 ± 0.2
	31.7 ± 2.0	91.0 ± 1.0	...	...	...	...	12.4 ± 0.4
	52.2 ± 1.5	8.3 ± 1.1	...	...	...	...	66.1 ± 0.4
6H-3	18.1 ± 0.5	0.8 ± 0.3	...	...	...	23.9 ± 0.3	...
	31.9 ± 1.6	91.0 ± 2.1	...	...	...	17.9 ± 0.4	...
	50.0 ± 1.1	8.2 ± 2.0	...	...	...	58.2 ± 0.2	...
6H-4	21.3 ± 0.5	0.7 ± 0.3	...	...	...	26.7 ± 0.2	...
	38.4 ± 0.9	92.0 ± 1.1	...	...	...	28.7 ± 0.2	...
	40.3 ± 0.5	7.3 ± 1.0	...	...	...	44.6 ± 0.3	...
5H	13.0 ± 0.5	0.6 ± 0.1	...	...	15.4 ± 0.6	...	...
	13.0 ± 0.5	85.2 ± 0.7	...	...	6.5 ± 0.5	...	...
	74.0 ± 1.0	14.2 ± 0.8	...	...	78.1 ± 0.3	...	...
3H-1	35.7 ± 0.7	1.8 ± 0.3	...	35.4 ± 0.5	...	...	...
	48.0 ± 0.2	93.6 ± 0.9	...	47.1 ± 0.8	...	...	...
	16.3 ± 0.5	4.6 ± 0.7	...	17.5 ± 1.2	...	...	...
3H-2	32.1 ± 0.5	...	...	32.2 ± 0.2	...	...	...
	48.8 ± 2.5	...	...	48.3 ± 0.2	...	...	...
	19.1 ± 2.1	...	...	19.5 ± 0.3	...	...	...
3H-3	12.4 ± 1.6	1.0 ± 0.6	...	31.3 ± 0.3	...	...	...
	82.9 ± 2.0	97.8 ± 0.6	...	59.0 ± 0.6	...	...	...
	4.7 ± 0.4	1.2 ± 0.2	...	9.7 ± 0.6	...	...	...
3H-4	33.1 ± 1.2	1.4 ± 0.4	30.3 ± 0.7	36.7 ± 0.4	...	...	...
	56.6 ± 1.7	94.6 ± 0.7	61.0 ± 0.8	50.0 ± 0.2	...	...	...
	10.3 ± 1.1	4.0 ± 0.6	8.7 ± 0.2	13.3 ± 0.1	...	...	...
1H	34.2 ± 1.3	...	...	34.0 ± 0.2	...	27.3 ± 0.2	...
	35.6 ± 3.7	...	...	36.9 ± 0.2	...	26.8 ± 2.0	...
	30.2 ± 4.0	...	...	29.1 ± 0.3	...	45.9 ± 2.0	...
4H	31.7 ± 1.7	...	...	32.6 ± 0.2	...	27.4 ± 0.2	...
	22.1 ± 3.2	...	...	31.9 ± 2.2	...	14.9 ± 0.1	...
	46.2 ± 4.5	...	...	35.5 ± 2.4	...	57.7 ± 0.3	...

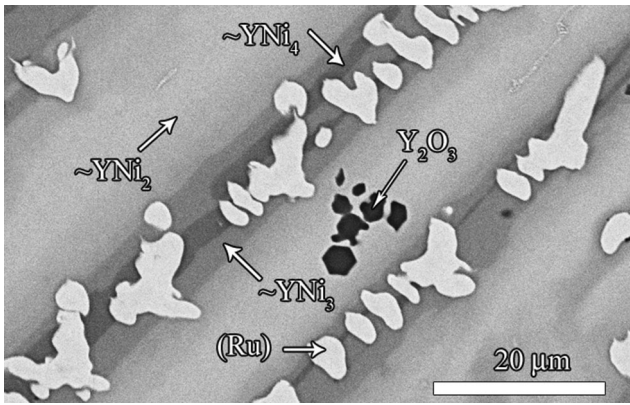


**Fig. 5** Scanning electron microscope backscattered electron image (SEM-BSE) image of as-cast nominal Ni<sub>7</sub>:Ru<sub>72</sub>:Y<sub>21</sub> (at.%) (Sample 12), showing (Ru) dendrites (light), (Ru) +  $\sim YRu_2$  (dark) eutectic structure and  $\sim YNi_2$  (medium)

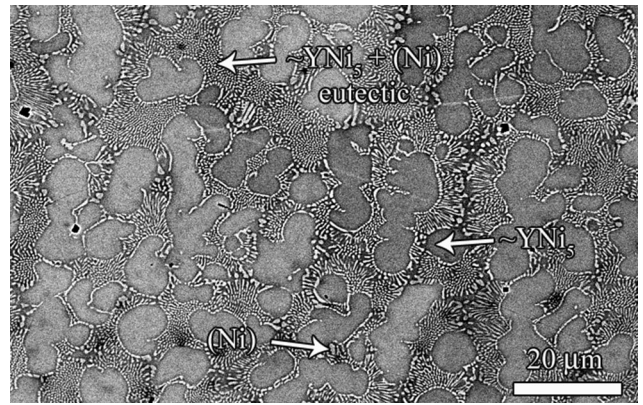


**Fig. 6** SEM-BSE image of as-cast nominal Ni<sub>54</sub>:Ru<sub>45</sub>:Y<sub>1</sub> (at.%) (Sample 2), showing very cored (Ru) dendrites (light), (Ni) (medium) and small areas of (Ni) (discrete) +  $\sim YNi_5$  (dark) eutectic structure

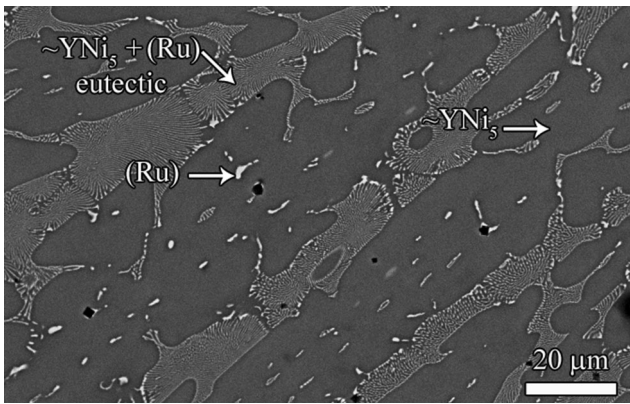




**Fig. 7** SEM-BSE image of as-cast nominal Ni<sub>38</sub>:Ru<sub>42</sub>:Y<sub>20</sub> (at.%) (Sample 6), showing primary (Ru) dendrites (very light),  $\sim$ YNi<sub>2</sub> needles (light),  $\sim$ YNi<sub>3</sub> (medium) and  $\sim$ YNi<sub>4</sub> (dark). The very darkest phase is Y<sub>2</sub>O<sub>3</sub>, or holes left after it was removed on sample preparation



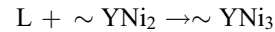
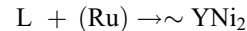
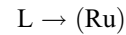
**Fig. 9** SEM-BSE image of as-cast nominal Ni<sub>76</sub>:Ru<sub>13</sub>:Y<sub>11</sub> (at.%) (Sample 13), showing  $\sim$ YNi<sub>5</sub> dendrites (dark) and  $\sim$ YNi<sub>5</sub> + (Ni) (light) eutectic structure



**Fig. 8** SEM-BSE image of as-cast nominal Ni<sub>69</sub>:Ru<sub>16</sub>:Y<sub>15</sub> (at.%) (Sample 5), showing  $\sim$ YNi<sub>5</sub> (dark dendrites) and  $\sim$ YNi<sub>5</sub> + (Ru) (light) eutectic structure

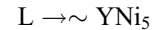
were two peritectic reactions forming large needles of  $\sim$ YNi<sub>2</sub> (sometimes pushing the dendrites aside), and  $\sim$ YNi<sub>3</sub>. The  $\sim$ YNi<sub>2</sub> phase had a much wider solubility than in the redrawn isothermal sections.<sup>[9,10]</sup> At higher magnifications, another phase was observed, and all phases had distinct boundaries (Fig. 7), indicating distinct phases rather than coring. The small dark phase areas of  $\sim$ YNi<sub>4</sub> would have meant that the EDX analyses were affected by the surrounding phases, so their analyses are not reported. There were also lighter contrast regions within the  $\sim$ YNi<sub>2</sub> needles, assumed to be  $\sim$ YNi<sub>2</sub> with higher Ru content, which solidified before the  $\sim$ YNi<sub>2</sub> with lower Ru content, with the lightest being remnant (Ru) dendrites (i.e. an incomplete peritectic reaction). The  $\sim$ YNi<sub>2</sub> solidified at a higher temperature than in the Ni-Y binary, because of the higher Ru content, and the direction of slope of the liquidus is consistent with the phase contrasts and analyses (albeit not accurate).

Thus, the deduced solidification reactions are:



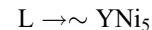
**3.1.4 Nominal Ni<sub>69</sub>:Ru<sub>16</sub>:Y<sub>15</sub> (at.%, Sample 5.** Nominal Ni<sub>69</sub>:Ru<sub>16</sub>:Y<sub>15</sub> (at.%) (Sample 5) was mostly dendrites of  $\sim$ YNi<sub>5</sub> with a fine lamellar eutectic structure comprising  $\sim$ YNi<sub>5</sub> and (Ru) (Fig. 8). The light phase was much too fine for accurate analysis, which was shown by the large errors (up to  $\pm 2.0$  at.%), and should have had a much higher Ru content.

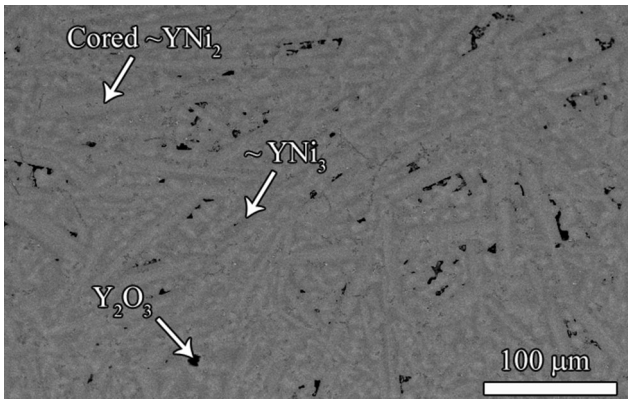
The solidification sequence was:



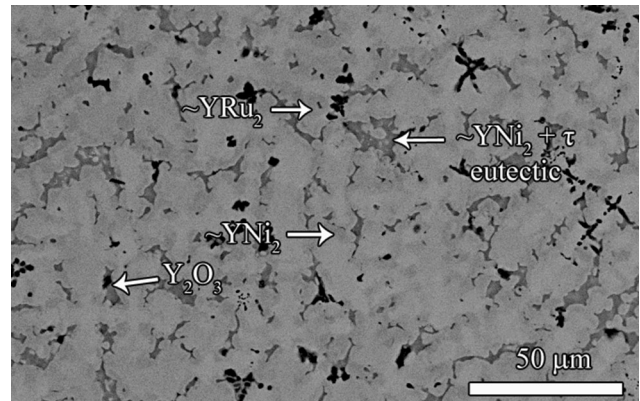
**3.1.5 Nominal  $\approx$ Ni<sub>76</sub>:Ru<sub>13</sub>:Y<sub>11</sub> (at.%, Sample 13.** Nominal  $\approx$ Ni<sub>76</sub>:Ru<sub>13</sub>:Y<sub>11</sub> (at.%) (Sample 13) had  $\sim$ YNi<sub>5</sub> dendrites of slightly different BSE contrasts and compositions, and a fairly coarse lamellar eutectic structure (Fig. 9). There was also fine precipitation in the dendrites. The dendrite analyses were similar, with the differences deriving from different local dendrite compositions on solidification and varying amounts of precipitation within. These effects were caused by the  $\sim$ YNi<sub>5</sub> phase having a very sloping solvus, so the lighter dendrites had slightly more Ru and Y, which would account for the large errors. Both of the eutectic components were too fine to accurately analyse individually, but the overall analysis of the univariant binary eutectic was obtained (Table 2).

The solidification sequence was:

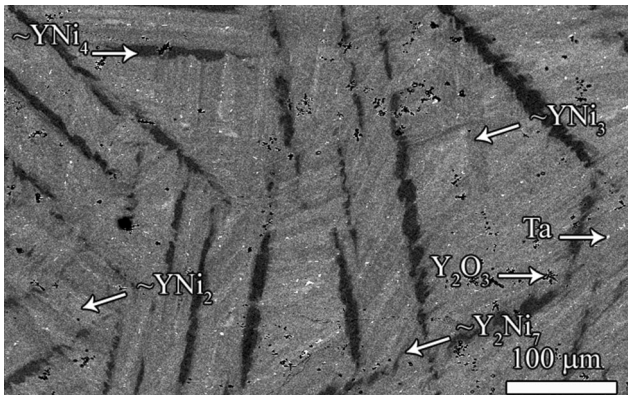




**Fig. 10** Low magnification SEM-BSE image of as-cast nominal  $\text{Ni}_{61}:\text{Ru}_{10}:\text{Y}_{29}$  (Sample 8), showing cored  $\sim\text{YNi}_2$  dendrites (light) and  $\sim\text{YNi}_3$  (medium), with  $\text{Y}_2\text{O}_3$  particles (dark)



**Fig. 12** SEM-BSE image of as-cast nominal  $\text{Ni}_{20}:\text{Ru}_{45}:\text{Y}_{35}$  (at.%) (Sample 3), showing  $\text{Y}_2\text{O}_3$  (dark),  $\sim\text{YRu}_2$  inner dendrites (light),  $\sim\text{YNi}_2$  outer dendrites (slightly darker) in a sparse eutectic structure of  $\sim\text{YNi}_2 + \tau$  (medium). The very darkest regions are holes left by  $\text{Y}_2\text{O}_3$  falling out



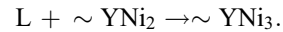
**Fig. 11** SEM-BSE image of as-cast nominal  $\text{Ni}_{70}:\text{Ru}_3:\text{Y}_{27}$  (at.%) (Sample 16), showing  $\sim\text{YNi}_4$  (dark),  $\sim\text{Y}_2\text{Ni}_7$  (medium dark),  $\sim\text{YNi}_3$  (medium), and  $\sim\text{YNi}_2$  (light). Darkest regions are holes where  $\text{Y}_2\text{O}_3$  was removed on sample preparation, and the very lightest regions are contamination from Ta



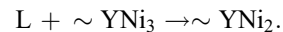
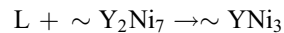
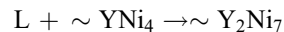
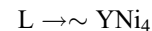
**3.1.6 Nominal  $\approx\text{Ni}_{81}:\text{Ru}_{10}:\text{Y}_9$  (at.%), Sample 7.** Nominal  $\sim\text{Ni}_{81}:\text{Ru}_{10}:\text{Y}_9$  (at.%) (Sample 7) was similar to  $\sim\text{Ni}_{76}:\text{Ru}_{13}:\text{Y}_{11}$  (at.%) (Sample 13), with the same solidification sequence, and precipitation within the dendrites. The true dendrite phase composition should be extrapolated away from (Ni) (which precipitated within), giving the phase to be  $\sim\text{YNi}_5$  (also confirming the  $\sim\text{YNi}_5$  phase in Sample 2).

**3.1.7 Nominal  $\approx\text{Ni}_{61}:\text{Ru}_{10}:\text{Y}_{29}$  (at.%), Sample 8.** In nominal  $\sim\text{Ni}_{61}:\text{Ru}_{10}:\text{Y}_{29}$ , the darkest phase was  $\text{Y}_2\text{O}_3$  (Fig. 10) and in some regions there was high porosity associated with the last phase to solidify. The  $\sim\text{YNi}_2$  needles formed first, followed by  $\sim\text{YNi}_3$ , and distinct interfaces between  $\sim\text{YNi}_2$  and  $\sim\text{YNi}_3$  were seen at higher magnification.

Ignoring the  $\text{Y}_2\text{O}_3$ , the solidification sequence was:



**3.1.8 Nominal  $\text{Ni}_{70}:\text{Ru}_3:\text{Y}_{27}$  (at.%), Sample 16.** Ignoring the light contrast contamination which filled some of the holes after polishing nominal  $\sim\text{Ni}_{70}:\text{Ru}_3:\text{Y}_{27}$  (at.%) (Sample 16) and the prior  $\text{Y}_2\text{O}_3$  phase, most of which had fallen out during sample polishing, leaving holes, there were four phases present (Fig. 11). The first phase to form,  $\sim\text{YNi}_4$ , could have been dendritic in morphology, although the subsequent peritectic reaction removed most of the outline, leaving an irregular needle-like appearance. The phase identification was achieved by comparison to the isothermal section of Sokolovskaya et al.<sup>[9]</sup> and by assuming that the binary Ni-Y phases extended into the ternary at constant Y content. The solidification sequence agreed with the peritectic cascade of phases reported in the Ni-Y binary,<sup>[5]</sup> and ignoring  $\text{Y}_2\text{O}_3$ , was:



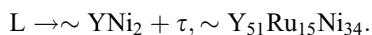
The  $\sim\text{Y}_2\text{Ni}_7$  and  $\sim\text{YNi}_2$  phases were too small to analyse accurately, giving large errors, and the analyses were made more Ni-rich by the surrounding higher Ni-content phases.

**3.1.9 Nominal  $\text{Ni}_{19}:\text{Ru}_{46}:\text{Y}_{35}$  (at.%), Sample 3.** There were some oxide particles in the nominal  $\sim\text{Ni}_{19}:\text{Ru}_{46}:\text{Y}_{35}$  (at.%) alloy (Sample 3), and the main dendrites had an inner composition of  $\text{Y}_{33}:\text{Ru}_{55}:\text{Ni}_{12}$  (at.%), and an outer composition of  $\sim\text{Y}_{24}:\text{Ru}_{44}:\text{Ni}_{32}$  (at.%). There were minor amounts of a two-phase interdendritic region of overall composition  $\sim\text{Y}_{51}:\text{Ru}_{15}:\text{Ni}_{34}$  (Fig. 12), where the contrast of one phase was similar to the outer dendrite. In some places, the



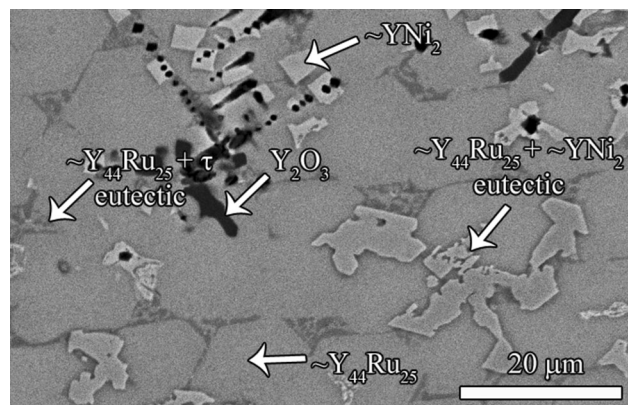
dendrites appeared cored, whereas in others, there was a distinct interface between the  $\sim Y_{33}:Ru_{55}:Ni_{12}$  and  $\sim Y_{24}:Ru_{44}:Ni_{32}$  (at.%). Both of these compositions, even with the relatively high errors ( $\pm 3$  at.% for the most Ni-rich component, and  $\pm 2$  at.% for the most Ru-rich component) were on the  $\sim YRu_2$  to  $\sim YNi_2$  transect, and fairly close to the limits of the  $\sim YRu_2$  and  $\sim YNi_2$  phases.<sup>[7,9]</sup> The high errors in Ni and Ru contents are consistent with coring in the Ni and Ru directions, and the low errors in Y are consistent with the phases having constant Y content. In the absence of good x-ray data, the phases could only be deduced by morphology and composition. The  $\sim YNi_2$  phase solidified as faceted dendrites with 48.3 at.% Ru (Sample 1) (Fig. 16) and 35.7 at.% Ru (Sample 4) (Fig. 17), faceted crystals with 49.8 at.% Ru (Sample 11) (Fig. 13), needles as a secondary phase with 46.1 at.% Ru (Sample 6) (Fig. 7), and needles then dendrites with 14.4 at.% Ru (Sample 8) (Fig. 10). Thus, for higher Ru contents,  $\sim YNi_2$  tended to solidify with a more faceted morphology, and with lower Ru contents, as dendrites. Here, the outer phase comprised 43.7 at.% Ru, which should have given a more faceted appearance, if it was  $\sim YNi_2$ . However, the phase was growing on a fair proportion of pre-existing  $\sim YRu_2$ , and so would have taken that shape initially. Thus, the two compositions and different contrasts were deduced to be inner dendrites of  $\sim YRu_2$  (of  $\sim 55.4$  at.% Ru). Since the analyses of the interdendritic region were actually of a sparse eutectic structure, which comprised mainly the darker component (lower atomic number contrast), the analysed composition of that component must lie near the univariant binary eutectic. However, since the overall analysis of this eutectic had large error bars (due to only small areas being available for analysis, and its univariant quality) and were near to the reported composition of  $\sim Y_5Ru_5Ni_2$ ,<sup>[9]</sup> which here is called  $\tau$ , ( $\sim Y_{51}Ru_{15}Ni_{34}$  (at.%)), the darker component was taken to be  $\tau$ . Comparison with the isothermal section<sup>[9]</sup> shows that the overall composition of the univariant binary eutectic,  $\sim Y_{51}:Ru_{15}:Ni_{34}$ , was in the two-phase region of  $\tau + \sim YNi$ , but the sparse component had the same contrast as  $\sim YNi_2$ , and so is taken to be this phase.

Ignoring the  $Y_2O_3$  phase, the sequence on solidification was:



### 3.1.10 Nominal $\approx Ni_{10}:Ru_{31}:Y_{59}$ (at.%), Sample 11.

The microstructure of Sample 11, nominal  $\sim Ni_{10}:Ru_{31}:Y_{59}$  (at.%), was complex and there appeared to be two different primary phases, ignoring  $Y_2O_3$ . The yttrium oxide solidified first and acted as a nucleation site locally for either of the next phases, showing that the boundary between the  $\sim YNi_2$  and  $\sim Y_{44}Ru_{25}$  liquidus surfaces was very close to the overall composition of the sample. In some places,  $\sim YNi_2$  formed on the oxide as regular, almost square, faceted blocks (top left of Fig. 13), and next, faceted  $\sim Y_{44}Ru_{25}$  formed, with a final univariant binary

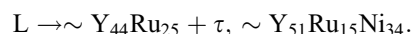
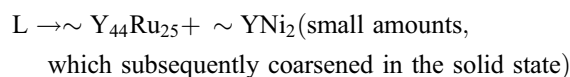
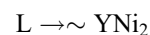


**Fig. 13** SEM-BSE image of as-cast nominal  $Ni_{10}:Ru_{31}:Y_{59}$  (at.%) (Sample 11), showing  $Y_2O_3$  dendrites (very dark), faceted  $YNi_2$  (light) and  $Y_{44}Ru_{25}$  faceted dendrites (medium contrast) with a coarse  $\sim Y_{44}Ru_{25} + \sim YNi_2$  eutectic structure, and fine  $\sim Y_{44}Ru_{25} + \tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$  (medium dark) eutectic structure

eutectic reaction. The oxide was ignored for phase diagram considerations. The EDX analyses (Table 2) had unacceptably high errors for  $\sim YNi_2$ , although the light phase appeared large enough to analyse without collecting any x-rays from the surrounding phases. This would be consistent with a wider phase field in the Y direction and coring on solidification, i.e. the Ru direction. The overall composition of the univariant binary eutectic was close to the ternary  $\sim Y_5Ru_5Ni_2$  phase,<sup>[9]</sup> and one eutectic phase was clearly  $\sim Y_{44}Ru_{25}$ , as it was associated with the faceted blocks. The composition of the second eutectic phase was roughly estimated by extrapolating from the known (by EDX analysis) eutectic phase,  $\sim Y_{44}Ru_{25}$ , through the overall composition of the eutectic, considering the proportions of the eutectic phases, to give  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$ . (This was very approximate, because it assumed the tie triangle of the univariant binary eutectic was a straight line.) The  $\sim YNi_2$  phase also had another morphology, which was more irregular (centre of Fig. 13), but still faceted, and in this morph, it was associated with the univariant binary eutectic. This was deduced to be from mainly solid state precipitation (which occurred after solidification was complete), after forming as a coarse eutectic structure with  $\sim Y_{44}Ru_{25}$ , and then the final, much finer,  $\sim Y_{44}Ru_{25} + \tau$  eutectic structure. This indicates that the  $\sim Y_{44}Ru_{25}$  solvus is sloping with temperature, allowing the  $\sim YNi_2$  to be precipitated subsequently in such a coarse morphology.

Ignoring the  $Y_2O_3$  phase, which is not part of the true solidification sequence for this composition, the solidification sequence for the regions where very regular  $\sim YNi_2$  formed (i.e. locally on that liquidus surface) is:

(1)

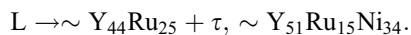


(2)

Alternatively, most of the sample solidified by:



$L \rightarrow \sim Y_{44}Ru_{25} + \sim YNi_2$  (small amounts,  
which subsequently coarsened in the solid state)

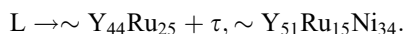
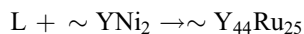


The average overall composition for the regions of solidification reaction 1 was  $5.5 \pm 0.2$  Ni,  $31.8 \pm 0.6$  Ru,  $62.7 \pm 0.5$  Y (at.%), with  $\sim YNi_2$  solidifying first, whereas the average overall composition for the regions of solidification reaction 2 was  $6.4 \pm 0.5$  Ni,  $31.9 \pm 0.6$  Ru,  $61.8 \pm 1.1$  Y (at.%), with  $\sim Y_{44}Ru_{25}$  solidifying first. Thus, the  $\sim YNi_2$  and  $\sim Y_{44}Ru_{25}$  liquidus surface boundary runs between these different local overall compositions. The solidification reaction that occurred only locally showed that the peritectic reaction forming  $\sim Y_{44}Ru_{25}$  from  $\sim YNi_2$  changed to a univariant binary eutectic at lower temperatures.

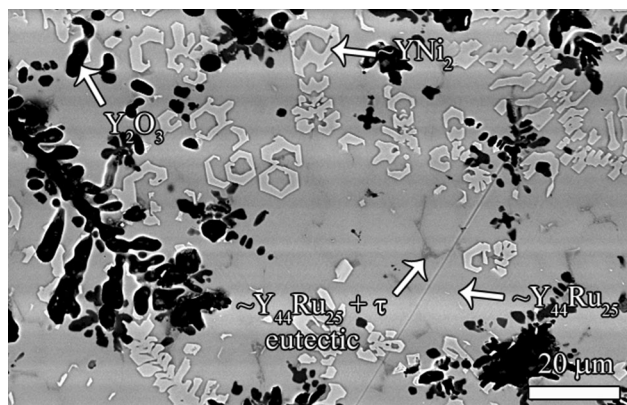
**3.1.11 Nominal  $Ni_6:Ru_{31}:Y_{63}$  (at.%), Sample 17.** Nominal  $Ni_6:Ru_{31}:Y_{63}$  (at.%) (Sample 17) was very similar to Sample 11, with the same phases and mostly the same morphologies, except that locally,  $\sim YNi_2$  formed definite faceted dendrites and hollow hexagons (Fig. 14). This confirmed that the boundary between the  $\sim YNi_2$  and  $\sim Y_{44}Ru_{25}$  liquidus surfaces must lie between these two compositions. The major primary phase was  $\sim Y_{44}Ru_{25}$  and the solidification reaction was the same as Reaction 2 for Sample 11.

**3.1.12 Nominal  $Ni_{16}:Ru_{23}:Y_{61}$  (at.%), Sample 18.** Nominal  $Ni_{16}:Ru_{23}:Y_{61}$  (at.%) (Sample 18) had a high proportion of  $Y_2O_3$ , but the true primary phase (of the Ni-Ru-Y system) was  $\sim YNi_2$ , which formed as faceted dendrites (Fig. 15). The next phase was  $\sim Y_{44}Ru_{25}$ , which formed long needles, and a univariant binary eutectic formed last. Although the morphology of the  $\sim Y_{44}Ru_{25}$  phase and  $\sim Y_{44}Ru_{25} + \tau$  eutectic structure appeared different in Samples 11 and 17, this is because the overall compositions of the univariant binary eutectic and phase proportions were different.

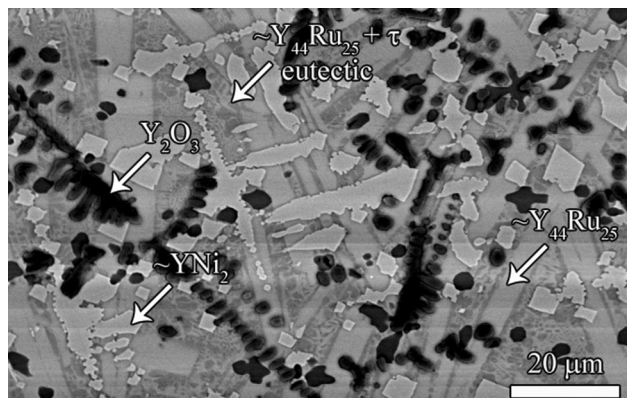
The solidification reactions were (ignoring the oxides):



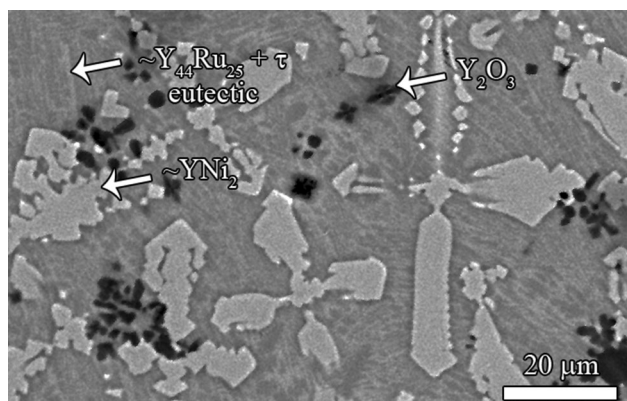
**3.1.13 Nominal  $Ni_{24}:Ru_{26}:Y_{50}$  (at.%), Sample 1.** The nominal  $Ni_{24}:Ru_{26}:Y_{50}$  (at.%) alloy (Sample 1) comprised primary  $\sim YNi_2$  as faceted dendrites in a univariant binary eutectic (Fig. 16; Table 2). Both of the eutectic phases were too small to accurately analyse individually, without collecting x-rays from the neighbouring phases. Comparison to the other univariant binary eutectics in the same region (Samples 1, 3, 11, 17 and 18) showed that the morphologies of these eutectics were similar, except for that of Sample 3, which was more



**Fig. 14** SEM-BSE image of as-cast nominal  $Ni_6:Ru_{31}:Y_{63}$  (at.%) (Sample 17), showing  $Y_2O_3$  dendrites (very dark), hollow hexagonal sections and faceted  $\sim YNi_2$  dendrites (light) and less-faceted coarse  $\sim Y_{44}Ru_{25}$  dendrites (medium contrast) with a small amount of fine  $\sim Y_{44}Ru_{25} + \tau, \sim Y_{51}Ru_{15}Ni_{34}$  (medium dark) eutectic structure



**Fig. 15** SEM-BSE image of as-cast nominal  $Ni_{16}:Ru_{23}:Y_{61}$  (at.%) (Sample 18), showing  $Y_2O_3$  dendrites (very dark), faceted  $\sim YNi_2$  dendrites (light) and  $\sim Y_{44}Ru_{25}$  needles (medium contrast) with  $\sim Y_{44}Ru_{25} + \tau, \sim Y_{51}Ru_{15}Ni_{34}$  (medium dark) eutectic structure



**Fig. 16** SEM-BSE image of as-cast nominal  $Ni_{24}:Ru_{26}:Y_{50}$  (at.%) (Sample 1), showing  $\sim YNi_2$  faceted dendrites (light) in a  $\sim Y_{44}Ru_{25}$  (medium) +  $\tau, \sim Y_{51}Ru_{15}Ni_{34}$  (medium dark) eutectic structure, with the darkest phase being yttrium oxide



sparse, indicating that Samples 1, 11, 17 and 18 had the same univariant binary eutectic. This gave the eutectic here as  $\sim Y_{44}Ru_{25} + \tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$ , whereas Sample 3 had a different univariant binary eutectic:  $\sim YNi_2 + \tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$ .

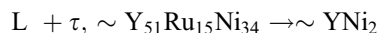
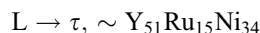
Ignoring the oxides (which formed first, and are not part of the ternary system), the deduced solidification sequence was:



The latter was a ternary invariant transition reaction.

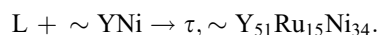
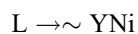
**3.1.14 Nominal  $Ni_{41}:Ru_{16}:Y_{43}$  (at.%), Sample 4.** The alloy of nominal composition  $Ni_{41}:Ru_{16}:Y_{43}$  (Sample 4) had faceted and apparently cored dendrites of  $\sim YNi_2$  (Fig. 17). However, if cored, the insides of the dendrites should have been lighter in BSE contrast, because they should have been more Ru-rich than the outer region. Since the dendrite inners were actually darker, they were deduced to be a phase with less Ru than  $\sim YNi_2$ , and thus  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$ , since the alternative,  $\sim YNi$ , formed subsequently. Surrounding the faceted dendrites was a sparse univariant binary eutectic with  $\sim YNi$  as the major component, and the minor component was deduced by contrast to be  $\sim YNi_2$ .

Ignoring the oxide phases, the solidification sequence was:

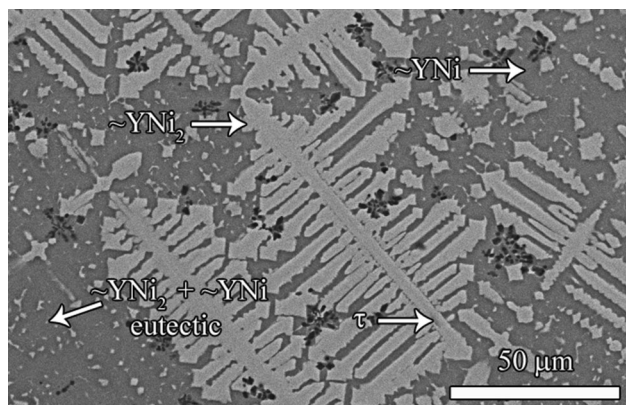


**3.1.15 Nominal  $Ni_{31}:Ru_{11}:Y_{58}$  (at.%), Sample 9.** The microstructure of nominal  $Ni_{31}:Ru_{11}:Y_{58}$  (at.%) (Sample 9) (Fig. 18) shows small, dark oxide dendrites, some of which were larger than usual, which had mostly been removed by polishing (being more brittle). There were medium grey contrast  $\sim YNi$  dendrites which sometimes formed on the oxide dendrites, followed by the light  $\tau$  matrix. The errors for the EDX analyses, especially for the  $\sim YNi$  and oxide phases, were unacceptably high, but their areas were small and the beam presumably spread more than expected.

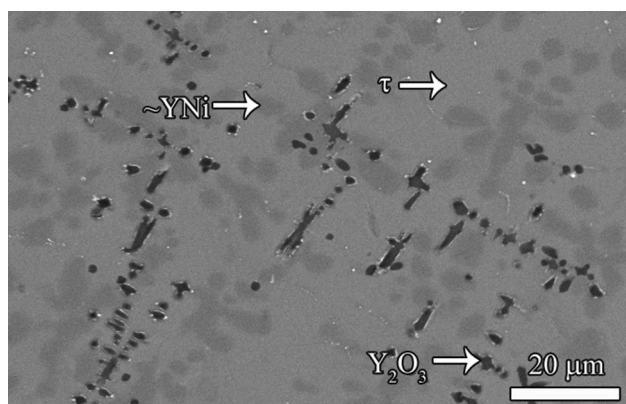
The solidification sequence was:



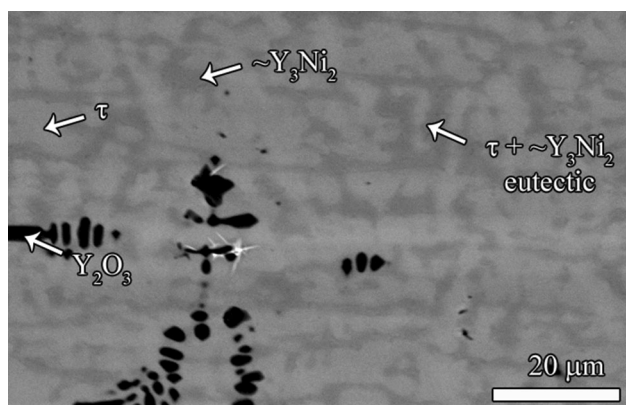
**3.1.16 Nominal  $Ni_{26}:Ru_8:Y_{66}$  (at.%), Sample 19.** Apart from the usual small  $Y_2O_3$  dendrites, nominal  $Ni_{26}:Ru_8:Y_{66}$  (at.%) (Sample 19) comprised a coarse globular eutectic structure, with the lighter component,  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$  almost appearing dendritic (Fig. 19). However, the fine scale of the morphology showed that this was a univariant binary eutectic, with very small dendrites of  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$



**Fig. 17** SEM-BSE image of as-cast nominal  $Ni_{41}:Ru_{16}:Y_{43}$  (at.%) (Sample 4), showing inner dendrites of  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$  (medium) surrounded by outer  $\sim YNi_2$  dendrites (light), in a  $\sim YNi_2 + \sim YNi$  (dark) eutectic structure, with darkest phase being yttrium oxide



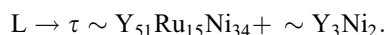
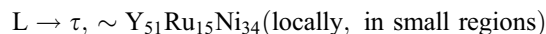
**Fig. 18** SEM-BSE image of as-cast nominal  $Ni_{31}:Ru_{11}:Y_{58}$  (at.%) (Sample 9), showing  $\sim YNi$  dendrites (medium) and  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$  (light), with the very dark dendrites being holes left by the removal of  $Y_2O_3$  during sample preparation



**Fig. 19** SEM-BSE image of as-cast nominal  $Ni_{26}:Ru_8:Y_{66}$  (at.%) (Sample 19), showing  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$  dendrites (light) in a globular  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34}$  (light) +  $\sim Y_3Ni_2$  (medium) eutectic structure, with very dark  $Y_2O_3$

occasionally solidifying before the eutectic. Thus, the alloy composition was just on the  $\tau$ -rich side of the  $\tau$ ,  $\sim Y_{51}Ru_{15}Ni_{34} + \sim Y_3Ni_2$  univariant binary eutectic valley, and the sample mostly solidified to the globular eutectic.

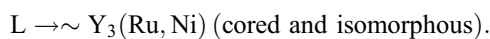
The solidification sequence was:



**3.1.17 Nominal Ni<sub>10</sub>:Ru<sub>12</sub>:Y<sub>78</sub> (at.%), Sample 14.** Unfortunately, the sample of nominal composition Ni<sub>10</sub>:Ru<sub>12</sub>:Y<sub>78</sub> (at.%) (Sample 14) because it is Y-rich was noticeably contaminated by tantalum, which formed almost pure (Ta) dendrites on the small Y<sub>2</sub>O<sub>3</sub> dendrites. The sample also formed a scale after manufacture and while in methanol. Although difficult to determine, because of the overlapping of the Ni and Y x-ray peaks with those of Ta, it was deduced that there was no Ta in the matrix (with the reasons given in the discussion).

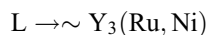
It was difficult to differentiate whether the rest of the microstructure was two separate phases, or coring, but the first component to form (after Y<sub>2</sub>O<sub>3</sub> and (Ta)) was the lighter component, originally assumed to be  $\sim Y_3Ru$ . The darker “interdendritic” regions were of the composition of  $\sim Y_3Ni$  at 600 °C,<sup>[8,9]</sup> and there was no discernable interface between them, indicating coring of an isomorphous phase,  $\sim Y_3(Ru,Ni)$ , rather than the two separate binary phases.

Thus, the solidification in the ternary was:

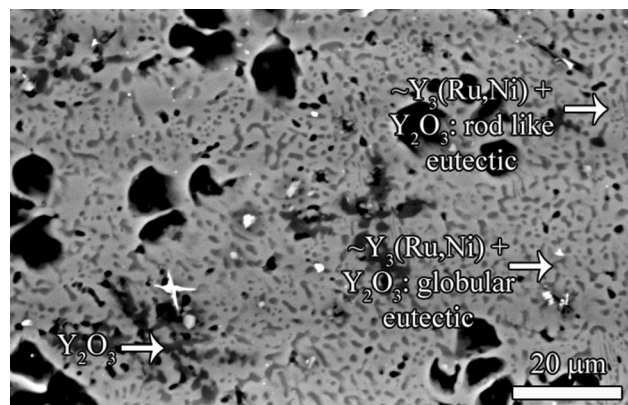


**3.1.18 Nominal Ni<sub>10</sub>:Ru<sub>11</sub>:Y<sub>79</sub> (at.%), Sample 10.** Sample 10, nominal Ni<sub>10</sub>:Ru<sub>11</sub>:Y<sub>79</sub> (at.%), was the only sample to have two different contrast dendrites of Y<sub>2</sub>O<sub>3</sub> and (Y), and these are thought to be (Y) in two different stages of oxidation (although these were a minor portion of the sample). There was also quite high Ta contamination, because of sample had a higher Y content. The major phase was dendritic  $\sim Y_3(Ru,Ni)$ , with a comparable solubility for Ni with that reported at 600 °C.<sup>[9]</sup> The rest of the sample was an irregular  $\sim Y_3(Ru,Ni) + (Y)$  univariant binary eutectic viewed at different orientations, similar to that in Fig. 20, consistent with the eutectic in the Ru-Y binary.<sup>[5]</sup> The (Y) in the eutectic structure had a different morphology from the small Y<sub>2</sub>O<sub>3</sub> dendrites, as though it was still being oxidised and falling out. There were also holes where the Y<sub>2</sub>O<sub>3</sub> had been removed during sample preparation.

Ignoring the obvious Y<sub>2</sub>O<sub>3</sub> and the Ta contamination associated with Y, the solidification sequence was:



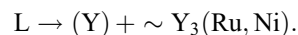
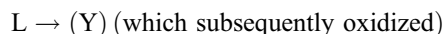
**3.1.19 Nominal Ni<sub>10</sub>:Ru<sub>6</sub>:Y<sub>84</sub> (at.%), Sample 15.** The sample of composition Ni<sub>10</sub>:Ru<sub>6</sub>:Y<sub>84</sub> (at.%) was also contaminated with Ta, but once again, the Ta was only found as small pure Ta particles in the sample, and did not dissolve in any of the other phases. This sample also formed



**Fig. 20** SEM-BSE image of as-cast nominal Ni<sub>14</sub>:Ru<sub>8</sub>:Y<sub>78</sub> (at.%) (Sample 15), showing two apparent eutectic structure morphologies (actually different orientations) of  $\sim Y_3(Ru,Ni) + Y_2O_3$  (dark): globular (mostly) and rod-like, and Y<sub>2</sub>O<sub>3</sub>

a scale after manufacture, and in methanol, and to a greater extent than Sample 14. There were holes where Y<sub>2</sub>O<sub>3</sub> had been pulled out during sample polishing, and some small dark Y<sub>2</sub>O<sub>3</sub> dendrites remained in the  $\sim Y_3(Ru,Ni) + Y_2O_3$  (originally (Y)) eutectic (Fig. 20). The eutectic structure had two apparent morphologies, with either globular or more needle-like discrete phases, which was an orientation effect. The phases were too small to be analysed individually and accurately. Although there was more of  $\sim Y_3(Ru,Ni)$ , its analysis was compromised by the (Y) particles in the eutectic structure, thus  $\sim Y_3(Ru,Ni)$  should have less Y than was found.

Given the high Y content of the sample, it is likely that (Y) formed first, then oxidized. The solidification reactions were deduced to be:

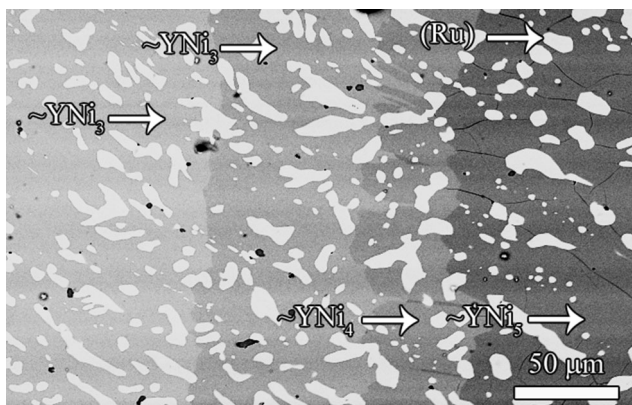


### 3.2 Heat Treated Samples

Unfortunately, rather than being annealed at 1000 °C as planned, the samples were actually annealed at 1200 °C for 1000 h. This meant that some of the samples experienced partial melting, and there was oxidation in the form of minor rounded oxides in the matrix, while Y loss was often severe. However, the results did give more information on the system.

**3.2.1 Nominal Ni<sub>38</sub>:Ru<sub>42</sub>:Y<sub>20</sub> (at.%), Sample 6H.** After heat treatment, nominal Ni<sub>38</sub>:Ru<sub>42</sub>:Y<sub>20</sub> (at.%), Sample 6H comprised four different regions of different microstructures, although some were the same phases as in the as-cast sample, which are reported in Table 4 as 6H-1 to 6H-4 from the outside inwards. These four different regions, with two intermediate layers, comprised (Ru) in matrices of  $\sim YNi_3$  of two different compositions,  $\sim YNi_4$  and  $\sim YNi_5$ , from the inside to the outside (Fig. 21). The last layer had cracks within  $\sim YNi_5$ , which usually ran between (Ru) regions. There were very small differences in the (Ru) contents in





**Fig. 21** SEM-BSE image of as-cast nominal  $\text{Ni}_{38}:\text{Ru}_{42}:\text{Y}_{20}$  (at.%) (Sample 6H) annealed at  $1200\text{ }^{\circ}\text{C}$  for 1000h, showing (Ru) (light) in darker matrices (from left to right): of  $\sim\text{YNi}_3$  of two different compositions,  $\sim\text{YNi}_4$  and  $\sim\text{YNi}_5$ , with the centre of the sample being towards the left

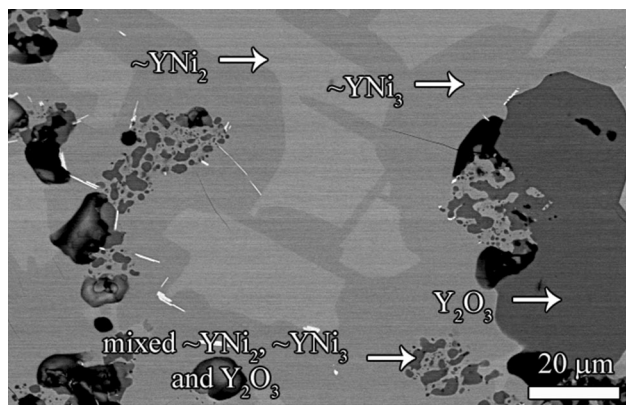
the different regions. Small regions of  $\text{Y}_2\text{O}_3$  were found throughout the sample, and were rounded and in a much smaller proportions than the  $\text{Y}_2\text{O}_3$  seen in the as-cast samples.

**3.2.2 Nominal  $\text{Ni}_{69}:\text{Ru}_{16}:\text{Y}_{15}$  (at.%) , Sample 5H.** The same phases, (Ru) and  $\sim\text{YNi}_5$ , as in the as-cast sample were found after heat treatment, but they had rounded and coarsened considerably. The sample had lost Ni.

**3.2.3 Nominal  $\text{Ni}_{19}:\text{Ru}_{46}:\text{Y}_{35}$  (at.%) , Sample 3H.** The as-cast microstructure of nominal  $\text{Ni}_{19}:\text{Ru}_{46}:\text{Y}_{35}$  (at.%) , Sample 3, had changed from the  $\sim\text{YRu}_2$  (inside)/ $\sim\text{YNi}_2$  (outside) dendrites with minor amounts of the univariant binary  $\sim\text{YNi}_2 + \tau$  eutectic, to regions of Si on the outside (which were ignored since this was contamination from the ampoules), (Ru) in  $\sim\text{YNi}_2$ ;  $\text{Y}_2\text{O}_3$  in  $\sim\text{YNi}_2$ ; and higher proportions of (Ru) variously in adjacent regions of  $\sim\text{YRu}_2$  and  $\sim\text{YNi}_2$  (all with minor amounts of rounded oxides).<sup>[18]</sup> In Table 4, these are denoted as 3H-1 to 3H-4 working inwards in the sample. In 3H-4, a coarsened eutectic-like structure of (Ru) +  $\sim\text{YRu}_2$  formed, consistent with the Ru-Y binary,<sup>[5]</sup> at lower temperatures in the ternary.

**3.2.4 Nominal  $\text{Ni}_{24}:\text{Ru}_{26}:\text{Y}_{50}$  (at.%) , Sample 1H.** The  $\sim\text{YNi}_2$  dendrites and  $\tau + \sim\text{Y}_{44}\text{Ru}_{25}$  univariant binary eutectic microstructure of as-cast  $\text{Ni}_{24}:\text{Ru}_{26}:\text{Y}_{50}$  (at.%) (Sample 1 and Fig. 16), had changed totally on heat treatment to blocks of  $\sim\text{YNi}_2$  in a matrix of  $\sim\text{YNi}_3$  with large rounded regions of  $\text{Y}_2\text{O}_3$ , and smaller mixed regions of  $\sim\text{YNi}_3$  and  $\text{Y}_2\text{O}_3$  (Fig. 22). The latter mixed regions (of composition:  $23.4 \pm 7.0$  Ni,  $19.4 \pm 1.6$  Ru,  $57.2 \pm 7.6$  Y (at.%) ) at least had melted, as indicated by the associated coarse porosity, and these regions were taken as the liquid composition. The sample had lost some Y and Ni, and comprised many large pores.

**3.2.5 Nominal  $\text{Ni}_{41}:\text{Ru}_{16}:\text{Y}_{43}$  (at.%) , Sample 4H.** As-cast  $\text{Ni}_{41}:\text{Ru}_{16}:\text{Y}_{43}$  (at.%) (Sample 4H) comprised  $\tau$  in  $\sim\text{YNi}_2$  dendrites in a sparse univariant binary eutectic of  $\sim\text{YNi}_2 + \sim\text{YNi}$ , whereas after heat treatment, there was severe reaction with the ampoule's silicon and much



**Fig. 22** SEM-BSE image of as-cast nominal  $\text{Ni}_{24}:\text{Ru}_{26}:\text{Y}_{50}$  (at.%) (Sample 1H) annealed at  $1200\text{ }^{\circ}\text{C}$  for 1000h showing blocks of  $\sim\text{YNi}_2$  (light) in  $\sim\text{YNi}_3$  (medium) with  $\text{Y}_2\text{O}_3$  (dark), and smaller mixed regions of  $\sim\text{YNi}_2$ ,  $\sim\text{YNi}_3$  and  $\text{Y}_2\text{O}_3$ , with some porosity (very dark)

oxidation. Portions in the centre of the sample, which were surrounded by coarse connected porosity had very similar microstructures to  $\text{Ni}_{24}:\text{Ru}_{26}:\text{Y}_{50}$  (at.%) (Sample 1H, Fig. 22), with  $\sim\text{YNi}_2$ ,  $\sim\text{YNi}_3$  and rounded  $\text{Y}_2\text{O}_3$  (although with no mixed regions). The sample had lost both Y and Ni.

## 4. Discussion

There were always problems with the (Y) phase being oxidised, despite keeping the samples in alcohol, and methanol was found to be better than ethanol. However, the higher Y content samples were even more problematic. The darkest phases were deduced as oxides because neither ruthenium nor nickel has been reported to have any discernible solubility in Y.<sup>[5]</sup> Thus, most of the samples had  $\text{Y}_2\text{O}_3$  and the true presence of (Y) was deduced by the microstructure, the overall composition of the alloy and the solidification sequence. Mostly, the oxide results were ignored in the interpretation of the ternary, although when interpreted as oxidized (Y), they were plotted ignoring the oxygen content (Fig. 23).

Another problem was the contamination of Ta, which was from contamination of the source Y material and was observed more in higher Y content samples. Yttrium was supplied by Goodfellow Metals Cambridge Limited, who stated that the supplied Y lumps could contain up to 300 ppm Ta, as well as other lesser impurities (Table 1) which were not found, being below the EDX detection limit. This problem was exacerbated, because in the energy dispersive x-ray spectra, significant peaks of Ta were overlapped by Ni and Y peaks, and the Ta peaks could only be discerned in the very high Y content alloys. It was deduced that there was no Ta in the matrix (since Y and Ta are nearly exclusively immiscible<sup>[5]</sup>) and thus the matrix compositions could be used in the phase diagram determination (although Ta is soluble in both (Ni) and (Ru), this higher Y content region is far away

from their solid solutions). This is further substantiated by considering the formation energies: the most negative formation energies were for the intermetallic compounds in the Ni-Y system,<sup>[21-23]</sup> (YNi<sub>3</sub>: -0.402 eV atom<sup>-1</sup>,<sup>[24]</sup> YNi<sub>2</sub>: -0.424 eV atom<sup>-1</sup>,<sup>[25]</sup> Y<sub>2</sub>Ni<sub>7</sub>: -0.380 eV atom<sup>-1</sup>,<sup>[26]</sup> YNi: -0.445 eV atom<sup>-1</sup><sup>[27]</sup>), and although the compounds in the Ni-Ta systems had negative formation energies,<sup>[21-23]</sup> they were less negative than those of the Ni-Y compounds (TaNi<sub>3</sub>: -0.366 eV atom<sup>-1</sup>,<sup>[28]</sup> Ta<sub>2</sub>Ni: -0.232 eV atom<sup>-1</sup>,<sup>[29]</sup> TaNi<sub>2</sub>: -0.340 eV atom<sup>-1</sup><sup>[30]</sup>). This was also the case for the reported Ru-Ta intermetallic compounds<sup>[21-23]</sup> (Ta<sub>3</sub>Ru: -0.215 eV atom<sup>-1</sup>; TaRu: -0.317 eV atom<sup>-1</sup>,<sup>[31]</sup> TaRu<sub>3</sub>: -0.196 eV atom<sup>-1</sup>) and the reported ternary compounds<sup>[21-23]</sup>, (YTaRu<sub>2</sub>: -0.335 eV atom<sup>-1</sup>; Y<sub>2</sub>NiRu: -0.361 eV atom<sup>-1</sup>).

Yttrium oxidized whereas the Ta did not, because yttrium has an exceptionally high affinity for oxygen, with a free energy of formation of the oxide of 1817 kJ mol<sup>-1</sup>, probably the highest of any element, and it also dissolves oxygen gas in relatively high concentrations.<sup>[32,33]</sup> The formation energies of the different structures of Y<sub>2</sub>O<sub>3</sub> (-3.846 eV atom<sup>-1</sup> <sup>[21-23,34]</sup> -3.809 eV atom<sup>-1</sup> <sup>[21-23,35]</sup> -3.784 eV atom<sup>-1</sup> <sup>[21-23,35]</sup> and -3.714 eV atom<sup>-1</sup> <sup>[21-23,36]</sup>) are all more negative than those of the most stable (i.e. most negative) tantalum oxide (Ta<sub>2</sub>O<sub>5</sub> at -3.186 eV atom<sup>-1</sup> <sup>[21-23,37]</sup>). Additionally, the amount of oxygen was limited in the closed environment of the arc-melter. When the Ti melted first as the oxygen getter, yttrium would have reacted next with the remaining oxygen (being in the larger proportion than tantalum), and subsequently would have left very little oxygen for Ta oxidation.

The phases were identified by comparing results with the isothermal section at 600 °C,<sup>[9]</sup> the component binary phase diagrams,<sup>[5]</sup> and comparing morphologies of the different phases. Limited XRD was undertaken, because by the time the samples had been fully analysed, they had oxidized to such an extent that XRD would have revealed a high proportion of the Y<sub>2</sub>O<sub>3</sub> oxide phase. Additionally, at the time of this work, there were insufficient data in the ICDD<sup>[38]</sup> and Karlsruhe<sup>[39]</sup> databases for the binary phases, and the patterns of at least some of the phases would have had to be modelled, then compared to the limited data. Even when XRD was undertaken, the spectra were of such a poor quality that they were not helpful.

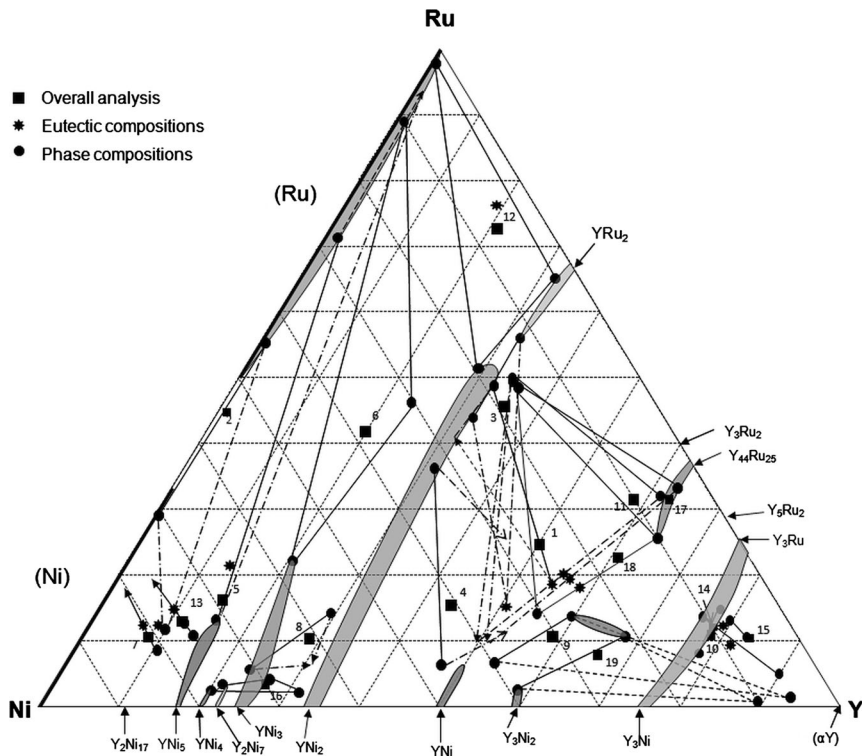
Some of the deductions are already described in the results of the individual alloys, and these were aided by plotting the compositions on a solidification projection (Fig. 23). For samples with Y<sub>2</sub>O<sub>3</sub> which was not considered part of the ternary, the lines between the phases are shown with dotted lines. The solidification temperatures of Samples 1 and 3 must have been fairly different, because the lines between the component phases cross. Although in an isothermal section (i.e. of a specific temperature), the tie-lines are forbidden to cross, since these are as-cast samples, if the solidification ranges are at different temperatures, then the lines between the phases can cross (they are probably not true tie-lines), as long as they lie at a fairly low angle to each other. The lines between the different phases of Samples 1 and 3 are consistent with Sample 3 solidifying at a higher temperature than Sample 1.

The wide solubility range of ~YNi<sub>2</sub> for Ru<sup>[7,9]</sup> was confirmed, and thus the phase was cored in the as-cast condition. The ~Y<sub>3</sub>Ni<sub>2</sub> phase was only found in Sample 10, which would be expected, since it only has a very small liquid surface, and so is unlikely to penetrate very far into the ternary. The same was true for ~Y<sub>2</sub>Ni<sub>7</sub>. The ~Y<sub>3</sub>Ru<sub>2</sub> and ~Y<sub>2</sub>Ni<sub>17</sub> phases were not found at all. This was partly because of limited penetration into the ternary in both solubility, and liquidus surface. However, not finding ~Y<sub>3</sub>Ru<sub>2</sub> could have been due to not having a sample composition near that phase. Not finding ~Y<sub>2</sub>Ni<sub>7</sub> is consistent with Sokolovskaya et al.<sup>[9-11]</sup> Most of the phases had very narrow ranges, except for: ~YNi<sub>2</sub>, ~YNi<sub>3</sub> (at least near the Ni-Y system), ~YNi and ~Y<sub>3</sub>(Ru,Ni). The binary phases penetrated into the ternary with constant Y content, agreeing with Sokolovskaya et al.<sup>[9-11]</sup> and being consistent with their reasoning.<sup>[9]</sup>

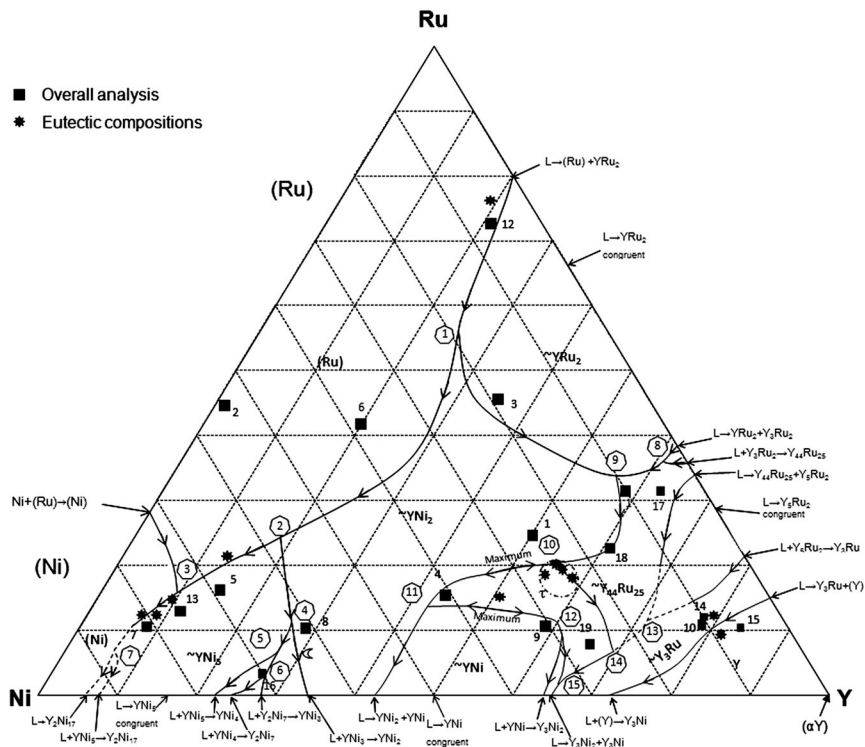
Assuming that the Ta contamination did not affect the other phases in which it did not dissolve, Sample 14 (Ni<sub>10</sub>:Ru<sub>12</sub>:Y<sub>78</sub> (at.%)) indicated that the ~Y<sub>3</sub>Ru and ~Y<sub>3</sub>Ni phases were continuous, at least on solidification, which is possible, since they both have the same *oP16* structure. However, no samples were made in that region, so this investigation cannot be conclusive on this. A miscibility gap for ~Y<sub>3</sub>(Ru,Ni) occurs at lower temperatures, since Sokolovskaya et al.<sup>[9-11]</sup> found two phases at 600 °C. Sample 14 (Ni<sub>10</sub>:Ru<sub>12</sub>:Y<sub>78</sub> (at.%)) disagrees with Samples 10 and 15, and had more contamination. However, Samples 10 and 15 had the univariant binary ~Y<sub>3</sub>(Ru,Ni) + (Y) eutectic. Although the analyses of this eutectic from the different samples were different, due to the small areas analysed and the one degree of freedom of this binary, the true analysis is near the overall composition of Sample 15, since this sample was mostly eutectic. This was taken into account when the liquidus surface (Fig. 24) was drawn.

When compared with the isothermal section at 600 °C of Sokolovskaya et al.<sup>[9]</sup> the phase widths of line compounds on the YNi<sub>2</sub> to YRu<sub>2</sub> transect of this study were in agreement<sup>[9]</sup> although wider than the subsequent compiled sections.<sup>[10,11]</sup> It would be expected that the phase widths at 600 °C would be narrower than on solidification, since solubility tends to decrease with decreasing temperature. The extensions of the binary phase into the ternary were: ~51 at.% Ru for ~YNi<sub>2</sub>; ~22 at.% Ru for ~YNi<sub>3</sub>; ~13 at.% Ru for ~YNi<sub>5</sub>; ~7 at.% Ru for ~YNi; and ~12 at.% Ni for ~YRu<sub>2</sub> and ~Y<sub>44</sub>Ru<sub>25</sub>. The ternary ~Y<sub>5</sub>Ru<sub>2</sub>Ni<sub>2</sub> phase of Sokolovskaya et al.<sup>[9-11]</sup> was seen in Samples 1, 3, 4, 9, 11, 18 and 19, but at a slightly different composition: ~Y<sub>51</sub>Ru<sub>15</sub>Ni<sub>34</sub> (at.%), and has been designated  $\tau$  here (for ternary phase).

The solidification reactions were deduced from the microstructures. The liquidus surface (Fig. 24) was drawn to be consistent with the phases analysed and identified, as well as with the solidification sequences and the accepted binary phase diagrams.<sup>[5]</sup> The overall compositions of the alloys had to lie on their primary phase liquidus surfaces, but the overall compositions of the univariant binary eutectics were not always accurate, and so did not lie at the junctions of their relevant liquidus surfaces, and those



**Fig. 23** Solidification projection of the Ni-Ru-Y system (at.%), with phases not present indicated by arrows, and numbers are the sample numbers



**Fig. 24** Liquidus surface projection of the Ni-Ru-Y system (at.%), with phases not present indicated by arrows, numbers are the sample numbers, and enclosed numbers are the reaction numbers

**Table 5 Invariant reactions of the Ni-Ru-Y system**

Reaction No.	Approximate liquid composition (at.%)	Invariant reaction
1	Ni <sub>19</sub> :Ru <sub>56</sub> :Y <sub>25</sub>	L + (Ru) + ~YRu <sub>2</sub> → ~YNi <sub>2</sub>
2	Ni <sub>58</sub> :Ru <sub>20</sub> :Y <sub>22</sub>	L + (Ru) + ~YNi <sub>2</sub> → ~YNi <sub>5</sub>
3	Ni <sub>75</sub> :Ru <sub>15</sub> :Y <sub>10</sub>	L + (Ru) → ~YNi <sub>5</sub> + (Ni)
4	Ni <sub>62</sub> :Ru <sub>12</sub> :Y <sub>26</sub>	L + ~YNi <sub>2</sub> + ~YNi <sub>5</sub> → ~YNi <sub>3</sub>
5	Ni <sub>66</sub> :Ru <sub>7</sub> :Y <sub>27</sub>	L + ~YNi <sub>3</sub> + ~YNi <sub>5</sub> → ~YNi <sub>4</sub>
6	Ni <sub>70</sub> :Ru <sub>3</sub> :Y <sub>27</sub>	L + ~YNi <sub>3</sub> + ~YNi <sub>4</sub> → ~Y <sub>2</sub> Ni <sub>7</sub>
7	Ni <sub>87</sub> :Ru <sub>7</sub> :Y <sub>6</sub>	L + (Ni) + ~YNi <sub>5</sub> → ~Y <sub>2</sub> Ni <sub>17</sub>
8	Ni <sub>3</sub> :Ru <sub>36</sub> :Y <sub>61</sub>	L + ~Y <sub>3</sub> Ru <sub>2</sub> → ~YRu <sub>2</sub> + ~Y <sub>44</sub> Ru <sub>25</sub>
9	Ni <sub>10</sub> :Ru <sub>34</sub> :Y <sub>56</sub>	L + ~YRu <sub>2</sub> → ~YNi <sub>2</sub> + ~Y <sub>44</sub> Ru <sub>25</sub>
10	Ni <sub>25</sub> :Ru <sub>21</sub> :Y <sub>54</sub>	L + ~YNi <sub>2</sub> → ~Y <sub>44</sub> Ru <sub>25</sub> + τ
Maximum	Ni <sub>33</sub> :Ru <sub>18</sub> :Y <sub>49</sub>	L + ~YNi <sub>2</sub> → τ
11	Ni <sub>44</sub> :Ru <sub>14</sub> :Y <sub>42</sub>	L + τ → ~YNi <sub>2</sub> + ~YNi
Maximum	Ni <sub>36</sub> :Ru <sub>14</sub> :Y <sub>50</sub>	L + τ → ~YNi
12	Ni <sub>28</sub> :Ru <sub>12</sub> :Y <sub>60</sub>	L + ~YNi + τ → ~Y <sub>3</sub> Ni <sub>2</sub>
13	Ni <sub>17</sub> :Ru <sub>12</sub> :Y <sub>71</sub>	L + ~Y <sub>5</sub> Ru <sub>2</sub> → ~Y <sub>44</sub> Ru <sub>25</sub> + ~Y <sub>3</sub> (Ru,Ni)
14	Ni <sub>24</sub> :Ru <sub>7</sub> :Y <sub>69</sub>	L + ~Y <sub>44</sub> Ru <sub>25</sub> → τ + ~Y <sub>3</sub> (Ru,Ni)
15	Ni <sub>32</sub> :Ru <sub>3</sub> :Y <sub>65</sub>	L + τ → ~Y <sub>3</sub> Ni <sub>2</sub> + ~Y <sub>3</sub> (Ru,Ni)

known to be inaccurate (due to their small areas) were only used as guidelines (Samples 1, 2, 3, 10 and 12). Although the univariant nature of these binary eutectic reactions would allow for changing overall compositions, this should not have moved the analysed compositions from the surface junctions, and so it is likely that the small eutectic regions were causing the inaccuracies. In order for Sample 8 to solidify as interpreted, with ~YNi<sub>2</sub> forming before ~YNi<sub>3</sub>, the addition of Ru raises the liquidus temperature for primary ~YNi<sub>2</sub> relative to that of primary YNi<sub>3</sub>. This is consistent with ~YNi<sub>2</sub> being stabilized by Ru, and so solidifying at higher temperatures than in the Ni-Y system. The directions of the reactions were drawn so that the reactions observed could be produced. For example, the microstructure of Sample 11 necessitated the L + ~YNi<sub>2</sub> → ~Y<sub>3</sub>Ru<sub>2</sub> + τ, ~Y<sub>51</sub>Ru<sub>15</sub>Ni<sub>34</sub> invariant reaction, and so the arrows were drawn accordingly. The coarsening of the ~YNi<sub>2</sub> + ~Y<sub>44</sub>Ru<sub>25</sub> eutectic structure by the large growth of ~YNi<sub>2</sub> in the solid state means that the ~Y<sub>44</sub>Ru<sub>25</sub> solvus retreats significantly at decreasing temperatures, which agrees with Sokolovskaya et al.<sup>[9-11]</sup> not reporting it at 600 °C below ~5 at.% Ni.

None of the samples had the Y<sub>5</sub>Ru<sub>2</sub> phase, and even though it forms congruently, it only has a small liquidus surface in the binary,<sup>[5]</sup> so lacking any other indication, it has been given a relatively small liquidus surface in the ternary. This and ~Y<sub>2</sub>Ni<sub>17</sub> were the only liquidus surfaces for which there was no indication from the current samples, and so they are shown by dotted lines in Fig. 24. The solidification reactions were either directly observed in the samples, or derived from the liquidus surface, and are shown in Table 5. In order to experience the reactions observed in the microstructures, the univariant equilibria L → τ + ~YNi<sub>2</sub> and L → τ + YNi must each have a maximum, which is consistent with the congruent solidification of YNi in the binary.<sup>[5]</sup>

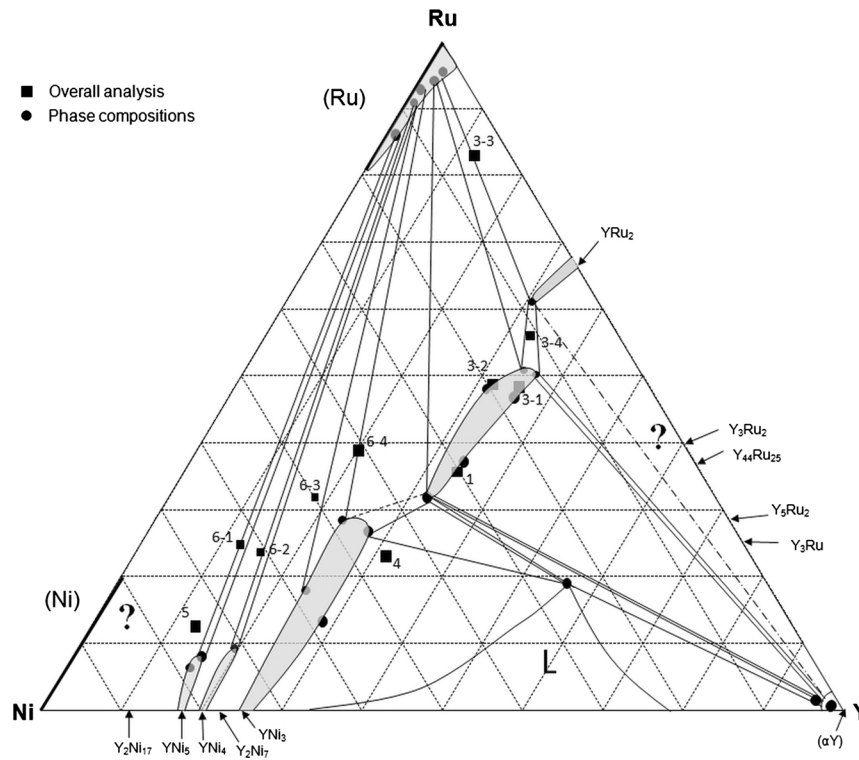
On heat treatment, despite precautions, the samples lost Y (Ni<sub>38</sub>:Ru<sub>42</sub>:Y<sub>20</sub> (at.%) to Sample 6H), or Ni (Ni<sub>69</sub>:Ru<sub>16</sub>:Y<sub>15</sub> (at.%) to Sample 5H), or both (Ni<sub>24</sub>:Ru<sub>26</sub>:Y<sub>50</sub> (at.%) to Sample 1; Ni<sub>19</sub>:Ru<sub>46</sub>:Y<sub>35</sub> (at.%) to Sample 3H). The Ni<sub>38</sub>:Ru<sub>42</sub>:Y<sub>20</sub> (at.%) alloy (Sample 6H) showed that the Y was lost on heat treatment, since the layers became less Y-rich towards the outside. There was also evidence that the ~YNi<sub>4</sub> layer formed by diffusion at the ~YNi<sub>3</sub>/~YNi<sub>5</sub> interface, since there were still small regions where this interface still existed (Fig. 20).

When the isothermal section at 1200 °C was plotted (Fig. 25), there was mainly (Ru), ~YRu<sub>2</sub>, ~YNi<sub>2</sub>, ~YNi<sub>3</sub>, ~YNi<sub>4</sub>, ~YNi<sub>5</sub> and (Y) (Y<sub>2</sub>O<sub>3</sub>). The other phases were missing because of their lower melting points (e.g. ~YNi<sub>2</sub>, ~YNi, ~Y<sub>3</sub>Ni<sub>2</sub> and ~Y<sub>3</sub>Ni), small penetration into the ternary (e.g. ~Y<sub>2</sub>Ni<sub>17</sub> and ~Y<sub>2</sub>Ni<sub>7</sub>), lack of an annealed sample near the phase compositions (e.g. (Ni), or both the last two reasons (e.g. ~Y<sub>3</sub>Ru<sub>2</sub>, ~Y<sub>44</sub>Ru<sub>25</sub>, ~Y<sub>5</sub>Ru<sub>2</sub> and ~Y<sub>3</sub>Ru). The mixed phase regions of Sample 1H were taken as the liquid composition at 1200 °C. The ~YNi<sub>3</sub> phase had a larger extension than at 600 °C,<sup>[9]</sup> which is consistent with solubility decreasing with temperature. The increased stability of ~YNi<sub>2</sub> agrees with the liquidus surface. The τ phase (~Y<sub>51</sub>Ru<sub>15</sub>Ni<sub>34</sub>) was not found at 1200 °C, indicating that it solidifies below 1200 °C.

## 5. Conclusions

Despite problems with oxidation of Y and its contamination by Ta, consistent interpretations were made using EDX results and phase morphologies. A solidification projection and a liquidus surface projection were drawn and were in agreement with the binary systems and the 600 °C isothermal section of Sokolovskaya et al. The ~YRu<sub>2</sub>, ~YNi<sub>2</sub> and





**Fig. 25** Isothermal section at 1200 °C of the Ni-Ru-Y system (at.%), with phases not present indicated by arrows, and numbers are the sample numbers

$\sim$ YNi<sub>3</sub> phases have wider solubilities than at 600 °C, which is expected. The binary phase extensions into the ternary were:  $\sim$ 51 at.% Ru for  $\sim$ YNi<sub>2</sub>;  $\sim$ 22 at.% Ru for  $\sim$ YNi<sub>3</sub>;  $\sim$ 13 at.% Ru for  $\sim$ YNi<sub>5</sub>;  $\sim$ 7 at.% Ru for  $\sim$ YNi; and  $\sim$ 12 at.% Ni for  $\sim$ YRu<sub>2</sub> and  $\sim$ 10 at.% Ni for  $\sim$ Y<sub>44</sub>Ru<sub>25</sub>. On solidification, the  $\sim$ Y<sub>3</sub>(Ru,Ni) phase was seen, which indicates a miscibility gap above 600 °C, to give  $\sim$ Y<sub>3</sub>Ru and  $\sim$ Y<sub>3</sub>Ni as separate phases, as observed by Sokolovskaya et al. Only the  $\sim$ Y<sub>3</sub>Ru<sub>2</sub> and  $\sim$ Y<sub>2</sub>Ni<sub>17</sub> phases were not found, due to limited penetration into the ternary, and  $\sim$ Y<sub>3</sub>Ni<sub>2</sub> and  $\sim$ Y<sub>2</sub>Ni<sub>7</sub> were also seen to have very limited extents. One ternary phase was found at  $\sim$ Y<sub>51</sub>Ru<sub>15</sub>Ni<sub>34</sub> (at.%), which is a slightly different composition than reported before. Heat treatment at 1200 °C gave the phases: (Ru),  $\sim$ YRu<sub>2</sub>,  $\sim$ YNi<sub>2</sub>,  $\sim$ YNi<sub>3</sub>,  $\sim$ YNi<sub>4</sub>,  $\sim$ YNi<sub>5</sub> and (Y). The higher formation temperature of  $\sim$ YNi<sub>2</sub> in the ternary was seen in both the liquidus projection and the isothermal section at 1200 °C and is due to the stabilization by Ru.

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