

## Solidification of Selected As-Cast Ni-Ru-Y Samples

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The Ni-Ru-Y system is being studied as a companion system to Al-Ru-Y for a potential new coating material. It is of interest because ruthenium has been shown to increase the corrosion resistance of stainless steels [1] and titanium alloys [2], and yttrium has been used in coating Ni-based alloys [3]. The Ni-Ru and Ni-Y binary phase diagrams are well established, but the reactions in Ru-Y are uncertain, although the phases are established [4]. The Ni-Y phase diagram is very complex with many phases [4]. No literature was found on the ternary system.

The samples were made by arc-melting the 99.9% pure elemental components, and titanium was used as an oxygen-getter. They were then sectioned, as near as possible into halves, mounted, and prepared for metallography. Analyses were undertaken using pure element standards in a Philips XL 30 ESEM equipped with an EDAX Phoenix EDS system.

Some of the alloys had small particles of  $Y_2O_3$ , which were assumed to be present before or in an early stage of melting, despite taking precautions (keeping the Y in alcohol). Since the oxide particles were in minor proportion, and have a very high melting point (2458°C [4]), they were ignored in the interpretation of the microstructures, despite the fact that they were sometimes nucleation sites. This was justified because attempts to interpret them as (Y), which then oxidised subsequently, gave impossible sequences of solidification reactions.

The  $Ni_{38}:Ru_{42}:Y_{20}$  (at. %) sample had primary (Ru), with ~10 at. % Ni. Next were two peritectic reactions forming the  $\sim YRu_2$  (actually of composition  $\sim Y_{24}Ru_{46}Ni_{30}$ ) and  $\sim Y_{20}Ru_{22}Ni_{58}$  phases respectively (Fig. 1). The  $\sim YRu_2$  phase was identified by its morphology and also from the smooth boundary formed around binary  $\sim YRu_2$  when the phase compositions from different samples were plotted on ternary paper.

Nominal  $Ni_{69}:Ru_{16}:Y_{15}$  was mostly a phase of composition  $\sim Y_{16}Ru_{13}Ni_{71}$  with small amounts of a eutectic comprising  $\sim Y_{16}Ru_{13}Ni_{71}$  and (Ru). At this stage, it is not known whether the major phase is a true ternary phase, or an extension of one of several Ni-Y phases in that region.

There were some oxide particles in the  $Ni_{19}:Ru_{46}:Y_{35}$  alloy, and the true primary phase was cored  $\sim YRu_2$  (the most Ru-rich composition being  $Y_{33}Ru_{55}Ni_{12}$ ), with minor amounts of an interdendritic phase of  $\sim Y_{51}Ru_{15}Ni_{34}$ . The overall composition did not lie on the tie-line because only the centres of the dendrites were analysed, and the dendrite edges had a higher nickel content.

The nominal  $Ni_{24}:Ru_{26}:Y_{50}$  alloy also had primary  $\sim YRu_2$  (with actual composition  $Y_{33}Ru_{48}Ni_{19}$ ) in a eutectic of overall composition  $Ni_{27}:Ru_{18}:Y_{55}$ . The two components of the eutectic were  $\sim YRu_2$ , with a slightly different composition from the primary phase (and hence slightly different contrast) and a grey phase. Both of these phases were too small to analyse accurately, without collecting X-rays from the neighbouring phases. However, the composition of the darker component can be extrapolated back towards the Ni-Y binary, directly away from the primary phase composition, so the phase is

probably  $\sim Y_3Ni$ . The solidification temperatures of this and the preceding alloy must have been fairly different, because the tie-lines cross. In an isothermal section, the tie-lines are forbidden to cross, but since these are as-cast samples, if the solidification ranges are different, then the tie-lines can cross, as long as they lie at a fairly low angle to each other.

The last alloy in the sequence,  $Ni_{41}:Ru_{16}:Y_{43}$ , also had dendrites of  $\sim YRu_2$ , with 33 at. % Ni (Fig. 2). The primary phase was the darker phase inside the dendrites, and this was too small to analyse accurately. However, the approximate composition could be derived by considering the offset of the overall composition against the tie-line joining the two analysed phase compositions, and the contrasts. Thus, the composition is likely to lie near the grey phase of the  $Ni_{19}:Ru_{46}:Y_{35}$  sample, at  $\sim Y_{51}Ru_{15}Ni_{34}$ . Most of the sample was  $\sim NiY$  (with 6 at. % Ru).

Analysis of the as-cast samples of the Ni-Ru-Y system has shown that the (Ru) phase extends to at least  $\sim 25$  at. % Ni in the ternary, but with little yttrium. The  $\sim YRu_2$  phase extends well into the ternary, at least to 33 at. % Ni. It was identified by its morphology and the fact that the compositions formed a smooth boundary when plotted on ternary paper. The other phases, nearer the Ni-Y binary, are difficult to determine without more samples, and structure determination. This has to be undertaken in later work.

## References

- [1] E. van der Lingen and R.F. Sandenbergh, *J. Corr. Sci.* 43 (2001) 577.
- [2] J.H. Potgieter et al., *ISIJ International*, 35 (1995) 197.
- [3] S. Grainger, ed., *Engineering Coatings – Design and Application*, Abington Pub., Cambridge, 1989.
- [4] Ed.-in-chief T.B. Massalski, eds., H. Okamoto et al., *Binary Alloy Phase Diagrams*, 2<sup>nd</sup> ed., Amer. Soc. Metals, Ohio, 1990.
- [5] The assistance of Mintek, DACST, PDI and the University of Botswana ORD is gratefully acknowledged.

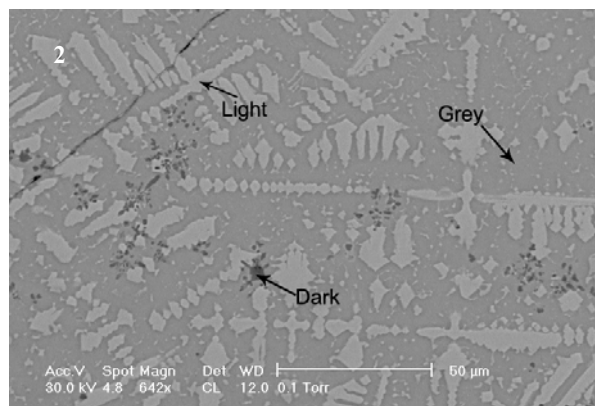
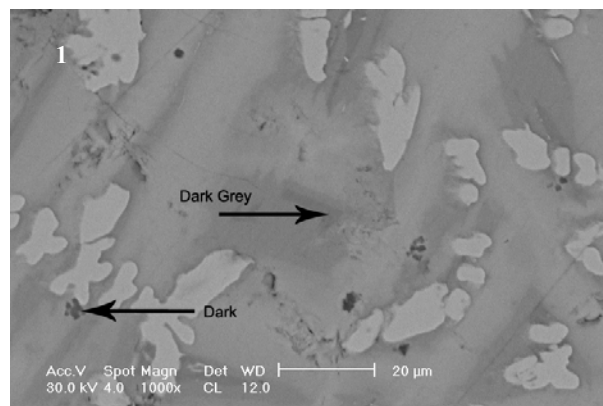


Fig. 1. Backscatter image of the  $Ni_{38}:Ru_{42}:Y_{20}$  (at. %) sample showing (Ru) dendrites (light), with  $\sim YRu_2$  (of composition  $\sim Y_{24}Ru_{46}Ni_{30}$ ) (medium),  $\sim Y_{20}Ru_{22}Ni_{58}$  (dark grey) and  $Y_2O_3$  (dark).

Fig. 2. Backscatter image of the  $Ni_{41}:Ru_{16}:Y_{43}$  sample showing  $\sim YRu_2$  dendrites (light) with darker centres ( $\sim Y_{51}Ru_{15}Ni_{34}$ ) in a  $\sim NiY$  (with 6 at. % Ru) matrix (grey), with very dark  $Y_2O_3$  particles.