Synthesis and characterization of lamellar and fibre-reinforced NiAl-Mo and NiAl-Cr

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Abstract. Directionally solidified (DS) alloys of the eutectic systems NiAl-10Mo and NiAl-34Cr (at.%) are potential candidates for high-temperature structural applications. Here, these alloys were first arc-melted and drop-cast. Thereafter, they were directionally solidified (DS) at growth rates of 20 and 80 mm/h while rotating at a fixed rotation speed of 60 revolutions per minute. Specimens of the DS alloys were tested in three-point-bending and uniaxial compression to obtain mechanical properties, including the ductile to brittle transition temperature (DBTT). For the NiAl-Cr system DBTT was found to be around 300 °C. Microstructural observations revealed that in the section perpendicular to the growth direction a uniform distribution of fibres was observed. The expected decrease of the fibre diameter with increasing growth rate was not observed. Instead, the fibre diameter slightly increased with increasing crystal growth rates. First compression tests were performed to get insights into the creep behaviour of these fibre-reinforced microstructures.

1. Introduction
The intermetallic compound NiAl possesses attractive properties for high temperature structural applications, e.g. high melting point, high oxidation resistance, a comparatively low ductile to brittle transition temperature (DBTT) and good thermal and electrical conductivity. Nevertheless, NiAl suffers from poor ductility and fracture toughness at room temperature (RT) and low strength and creep resistance at elevated temperature. Hence, substantial efforts have been made to enhance the mechanical properties through grain refinement, micro- and macro-alloying and the incorporation of second phase particles [1, 2].

Another way to increase ambient and high temperature strength is to employ fibre reinforcement. To avoid interface and debonding problems, intermetallics that were in-situ reinforced with refractory metals were investigated earlier, especially, eutectics produced by directional solidification [2, 3].
2. Experimental procedures

Alloys having a nominal composition of NiAl-10Mo and NiAl-34Cr (at.%) were prepared. First the alloying elements were weighed, placed in a copper crucible, and arc-melted under argon atmosphere. The arc-melted buttons were flipped and remelted five times to ensure homogeneity, after which the alloys were drop cast in a cylindrical copper mould 10 mm in diameter. The total weight loss was less than 0.05%. The cast ingots were directionally solidified (DS) according to the procedure given in [4] using two different growth rates, 20 and 80 mm/h.

The DS rods were cut transverse to the growth direction using an electro-discharge machine or a circular diamond saw. The samples were embedded in epoxy resin or conductive bakelite and prepared by standard metallographic methods (grinding to grit size 2400, polishing to 1µm). The NiAl-Mo samples were etched with a solution of 80% hydrochloric and 20% nitric acids [4], the NiAl-Cr samples with a solution of 18% HCl, 8% H$_2$O$_2$ and balance H$_2$O [5].

The metallographically prepared samples were examined by optical and scanning electron microscopy in the secondary electron (SE) image mode. The fibre spacing, fibre diameter and fibre density were analyzed with ImageJ and MATLAB.

Bending and compression tests were carried out in a Zwick electromechanical testing device equipped with a Maytec vacuum furnace, the former using specimens with a rectangular cross section (length of 30 mm and a support length of 25 mm) and the latter using specimens with a rectangular cross section of about 2 mm x 3 mm and a height of about 4.5 mm. The strain rate was approximately $10^{-3}$ s$^{-1}$. Tests on the NiAl-Mo alloy were carried out in a protective atmosphere, whereas NiAl-Cr was tested in air, which demonstrated the promising oxidation resistance of the latter. The direction of compression corresponded to the growth direction of the crystals, whereas bending was carried out perpendicular to the fibre axis. Hence, the fibres were loaded in tension and compression on either side of the neutral axis.

![Figure 1. SEM images of sections perpendicular to the growth direction for NiAl-10Mo grown at 80 mm/h (a) and NiAl-34Cr 20 mm/h (b), cuts parallel to the growth direction showing well-aligned fibres in NiAl-10Mo 20 mm/h (c) and misalignments at colony boundaries in NiAl-10Mo 20 mm/h (d) and NiAl-34Cr 80 mm/h (e).](image)

3. Results and discussion

The microstructure observed in the NiAl-X alloys perpendicular to the growth direction of the crystals shows the expected structure (figures 1 a and b), namely molybdenum and chromium fibres, respectively, embedded in a matrix containing mainly nickel and aluminum [4, 6, 7, 8]. The Mo fibres appear more uniform and are arranged in domains with a nearly hexagonal lattice, whereas the Cr-fibres seem to be less ordered and scatter more widely in diameter. In addition, the Cr-containing material exhibits a cellular solidification structure. The area fraction of the Cr-fibres is substantially higher than that of the Mo fibres, as expected from their compositions and the phase diagrams [2]. Table 1 summarizes characteristic properties of these structures. Some values are not consistent with the information available in the literature: for example,
one expects an increasing fibre diameter with decreasing growth rate [8]; here the opposite was observed. Figures 1 c, d and e show the microstructure parallel to the growth direction. Figure 1 c illustrates clearly that fibres with an aspect ratio of at least 100 were achieved. However, grain boundaries are visible as well (figures 1 d and e). The presence of grains with different fibre orientations clearly demonstrates that a single crystalline NiAl-matrix was not achieved, which was also confirmed by EBSD-analysis. This might be a possible reason for the mismatch between expected and observed relationship between growth rate and fibre size/spacing in table 1.

Table 1. Characteristic values of the fibre structure of NiAl-X

| Material      | Growth rate [mm/h] | Average fibre diameter [µm] | Area fraction [%] | Fibre density [µm⁻²] | Average fibre spacing [µm] | Theoretical density [g/cm³] |
|---------------|--------------------|------------------------------|-------------------|-----------------------|----------------------------|-------------------------------|
| NiAl-9Mo      | 20                 | 0.54                         | 13                | 0.85                  | 1.10                       | 6.29                          |
| NiAl-9Mo      | 80                 | 0.68                         | 12                | 0.39                  | 1.65                       | 6.29                          |
| NiAl-34Cr     | 20                 | 0.48                         | 38                | 3.48                  | 0.60                       | 6.31                          |
| NiAl-34Cr     | 80                 | 0.52                         | 37                | 2.67                  | 0.75                       | 6.31                          |

Figure 2(a) illustrates the temperature dependence of the strain at the outer tensile fibre in bending tests. At room temperature (RT) NiAl-Mo behaves in a completely brittle manner, whereas between 300 and 400°C it up to 5 times higher strain and 10 times higher ultimate stress values (Fig. 2(a)) were observed. NiAl-Cr grown at 20 mm/h more than doubles its strain value between 300 and 400°C, from 3.4 to 8.4%. Hence, the DBTT is around 300°C. All the other tested materials, excluding NiAl-Cr, 80 mm/h, show significant strains of more than 4% at 400°C. Therefore, the DBTT is expected to be around this temperature. Miracle [1] reported a DBTT of 200°C and 375°C for soft and hard oriented single NiAl crystals and between 325 and 625°C for polycrystalline NiAl. Hence, the DBTT of the present alloys is at the lower end of polycrystalline NiAl. It is also lower than the 675°C given by Bei and George [4] for NiAl-Mo tested in tension (as opposed to the bending tests performed here). Further, experiments have to be done to correlate the bending and tensile results, nevertheless, the values for DBTT obtained in this work are encouraging.

Figure 2(b) illustrates the temperature dependence of the achieved maximum stresses. In agreement with [1] the maximum stress peaks for all materials around the DBTT at approximately 2000 MPa and decreases towards both lower and higher temperatures to roughly
600 MPa around 600°C for NiAl-Mo grown at 80 mm/h and NiAl-Cr grown at the same speed, respectively. These strength values are consistent with [2, 8] and more than twice as high as that achieved by Zhong et al. [9] in tensile tests of ex-situ Al₂O₃ fibre-reinforced NiAl at 700°C, hence, confirming the notion that in-situ reinforcement is less prone to fibre delamination.

The creep performance achieved of the tested eutectic materials is shown in figure 3, which is a plot of creep rate vs. density-compensated creep stress. Stress exponents n between 7 and 10 were observed which is in good agreement with data reported by Miracle [1]. For comparison, the figure contains own measurements of compressive creep properties for a single crystalline Nickelbase superalloy CMSX4 in the [001] direction at 1050°C as well as values for polycrystalline NiAl at 750°C given in [10]. In comparison with polycrystalline NiAl, the creep performance of in-situ fibre reinforced NiAl is strongly enhanced, even though the former was tested at a much lower temperature. By contrast, the creep performances of our NiAl-X in-situ composites are already comparable with that of CMSX-4.

4. Conclusion
In summary, the tested materials possess comparatively low DBTTs of < 300°C and it appears as if our data merge with the SX superalloy’s creep response at application relevant low strain rates. These encouraging results have to be proven with further (long term) creep tests at even lower applied stresses, preferably using tensile specimens.

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