

Fabrication of rhenium nanowires by selective etching of eutectic alloys

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Abstract

Rhenium nanowires have been fabricated via directional solidification and selective etching of a eutectic alloy. A NiAl–1.5 at.%Re eutectic alloy was directionally solidified using a constant growth rate and temperature gradient, in the Bridgman-type directional solidification furnace. The selective dissolution of the NiAl matrix was achieved with a mixture of HCl:H₂O₂, and produced an anisotropic etching of the eutectic, with the favoured etching directions aligned in parallel. The corroded surface was dominated by long rhenium fibres (diameter ~400 nm), although shorter, and sometimes more rectangular wires were also observed in some sections. Digestion of the NiAl–Re eutectic in sulphuric acid, on the other hand, produced mainly long rhenium fibres of consistent shape and length. Both etching procedures might subsequently be applied for the preparation of nanodisc electrode arrays by embedding the obtained Re nanowires into a polymer and grinding until the wires are exposed. The reduction on the electrode area inherent in the use of such nanoelectrodes would allow a considerable increase in the signal-to-noise ratio, thus favouring the system for its application in analytical sensors. The use of rhenium in the electrode formation might also favour its application in high-temperature measurements.

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1. Introduction

Fabrication of nanostructures is a hot topic in current scientific research due to the potential uses of such species in nanotechnology [1]. The optical, chemical and mechanical properties of nanostructures are improved when compared to conventional materials, and open the possibility of their application in a wide variety of fields, such as high activity catalysts, chemical and biological sensors, and magneto-electronics and optoelectronics devices, among others [2]. Conventional methods for the fabrication of nanostructures include lithographic techniques, although such an approach often presents limited performance. Metallic

nanowires have been mainly fabricated by template-directed synthesis, involving either chemical or electrochemical deposition of the metal [3–6]. Thus, gold nanowires have been fabricated on polycarbonate templates by pulsed-laser deposition combined with electrochemical plating [3], generating nanowire arrays with a high aspect ratio and a diameter between 100 and 600 nm after dissolution of the carbonate template. Arrays of Ni nanowires with a diameter of 30 nm have been electrodeposited in alumina membranes [4,5]. Gold nanowires were also synthesised in silicon chips by electroreduction of tetrachloroaurate, yielding wires with diameters as low as 15 nm. However, the main disadvantage of template electrodeposition is the presence of impurities from side reactions. Another disadvantage of this method is the significant damage that can be produced on the nanostructures during template removal. To overcome these limitations,

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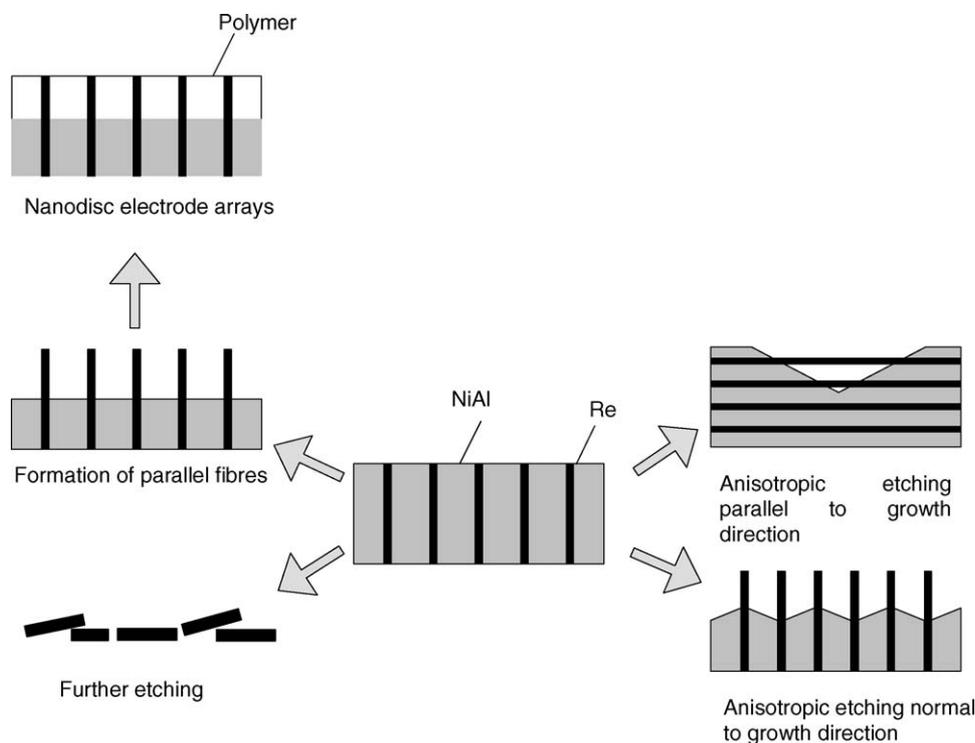


Fig. 1. Scheme of the road map followed for the production of nanowires and nanosensor arrays.

other techniques have been developed for the fabrication of nanowires. The need of a template for the deposition of nanostructures was obviated by use of microwave dielectric heating during the formation process [7]. This method was exploited for the formation of gold nanowires with a diameter of 20–100 nm, although such wires were only minor products in a mixture of gold nanoparticles and nanoplates. The vast amount of different structures obtained with this method proves its versatility, but complicates the applicability of the final product because of the complex and heterogeneous mixture of the resulting nanostructures (thus, their differences in shape, form and length make them incompatible for a single common application). An alternative technique for the fabrication of nanowires made use of binary alloys that were firstly electrodeposited on a template, after which one of the components was etched to leave nanowires of the remaining metal [8]. This method seemed appropriate for the production of large amounts of identical wires.

Overall, the main objective in nanotechnology is the fabrication of organised and controllably patterned materials with functional use in various technological processes [2]. Thus, for the fabricated nanowires to show reproducible patterns and characteristic within individual samples, a method must be developed that allows the production of self-organised nanostructures (SONS). These structures present identical physical characteristics and are well organised into the matrix, thus making them ideal candidates for use in arrays for nanosensing or nanoelectronic devices. The production of such SONS is presented in this work by use of directional solidification of eutectics. Directional solidification

of eutectics can yield highly ordered nanostructures with lamellar or fibrous shape depending on the system and the solidification parameters. Our idea was to produce fibrous eutectics in which elements such as rhenium, gold or platinum formed the minor eutectic phase. Nanowires of these metals could therefore be obtained from such eutectics after selective etching of the matrix. For this process to occur, the major phase must be poorly soluble in the fibrous phase and less noble (NiAl) [11]. From the possible NiAl–X systems, the NiAl–Re showed a fully eutectic microstructure with regular fibrous morphology, as desired for the proposed approach. Digestion of the resulting NiAl–Re eutectic in an appropriate oxidising solution, and without application of an external voltage, would result in the dissolution of both Ni and Al elements as Al(III) and Ni(II) ions, whereas Re would stay intact at that potential range, according to the E–pH diagram for each metal [9]. The choice of oxidising solution and/or digestion time would result in different dissolution range for all three components, as schematised in Fig. 1.

2. Materials and methods

2.1. Preparation of eutectics

As a starting material, nickel (99.97 wt.%), electrolytic aluminium (99.9999 wt.%) and rhenium pellets (99.9 wt.%) were used for the alloy preparation. Pre-alloys were prepared by induction melting under inert atmosphere and drop cast-

ing into a cylindrical copper mould. Subsequently, the as cast ingots were fitted into alumina crucibles and directionally solidified in a Bridgman type crystal growing facility. It consists of the crucible support, cooling ring and heating element (Tungsten net). The alumina crucible with the as-cast ingot was positioned in the furnace and heated up to $\sim 1700^\circ\text{C}$. After the material in the crucible was completely melted, the upper part with the heating element is slowly and uniformly shifted upwards, providing thus unidirectional heat extraction. This operation was controlled by a servomotor that enabled a speed range from 1 to 200 mm h^{-1} . The experiments were conducted at a temperature of $1690 \pm 10^\circ\text{C}$, a thermal gradient of approximately 40°C cm^{-1} and a growth rate of 30 mm h^{-1} . The microstructure of the obtained unidirectionally solidified NiAl–1.5 at.% Re eutectic exhibited fully eutectic morphology consisting of a cell structure with a mean cell diameter of 1.5 mm and a length covering the entire length of the rod-like sample. The mean diameter of the Re fibres in the eutectic cells was about 400 nm, while the mean inter fibre spacing was $3\ \mu\text{m}$. The fibre orientation was $\langle 1120 \rangle$ referring to the rod axis of the directionally solidified sample. The samples of the pure NiAl were cast as described above.

2.2. Production of nanowires

Re nanowires were obtained after a selective removal of the NiAl phase in the alloy. Three oxidising solutions were investigated for the optimal etching of NiAl: a solution containing 3.2% HCl and 3% H_2O_2 in distilled water, 5 M sulphuric acid solutions, and aqua regia. The eutectic alloy was cut in $1\text{ cm} \times 1\text{ cm} \times 0.1\text{ cm}$ cuboids, which were then immersed into the oxidising mixture for increasing periods of time (10 min to 24 h). The green solution obtained with this treatment was afterwards filtered using a glass vacuum filter unit with 200 nm pore size cellulose acetate membranes (Sartorius, Goettingen, Germany). Analysis of the filtered solution and membrane was performed by inductively coupled plasma optical emission spectrometry (ICP-OES) in order to calculate the total content of the three metals of interest (Ni, Al, and Re).

Scanning electron microscopy was performed using a Leo 1550 VP apparatus (Leo Elektronenmikroskopie GmbH, Oberkochen, Germany) fitted with an INCA Energy Dispersive System (EDS) (Oxford Instruments, Oxford, UK).

2.3. Measurement of corrosion potential

Measurements of free corrosion potentials (at open circuit) were carried out for pure Re and NiAl in aqua regia (concentrated HNO_3 and HCl in a 1:3 ratio), 5 M H_2SO_4 solutions and a mixture of 3.2% HCl and 3% H_2O_2 . A rhenium wire (diameter 0.5 mm) was immersed into each of the studied solutions and the corrosion potential measured versus a commercial Ag/AgCl reference electrode. For studies on the corrosion of NiAl, a $1\text{ cm} \times 1\text{ cm} \times 0.1\text{ cm}$ section was taken from a sample manufactured in house at the Department of Materials Technology (MPIE, Düsseldorf, Germany). The NiAl sample was immersed in the solutions and the potential measured accordingly. The potentials were read with a portable MXD-4660A Voltcraft voltmeter (XLSmess, Tübingen, Germany).

3. Results

3.1. Digestion of the NiAl–Re eutectic in a HCl:H₂O₂ mixture

For the NiAl matrix to be selectively dissolved, the etching solution must be acidic and only slightly oxidising, maintaining a corrosion potential close to 0 V to avoid the dissolution of the rhenium fibres [9]. Therefore, a mixture containing 3.2% HCl and 3% H_2O_2 was initially investigated [10]. The concentration of both HCl and H_2O_2 yielded the oxidation of the matrix, with the rhenium phase remaining in the solid, as confirmed by ICP-OES analysis of the recovered solution after filtration of the treated sample (Table 1). This digestion treatment produced an anisotropic etching of the matrix, which displayed hexagonal pits located on the same or parallel axis (Fig. 2). The rhenium fibres appeared distributed in cells throughout the sample. The observed fibres showed variable length and a diameter of $\sim 400\text{--}450\text{ nm}$, which correlates with the diameter of the Re fibres obtained after solidification in the eutectic cell [11]. However, not all the obtained fibres presented the same shape, depending on their position on the sample and therefore their exposure to the attacking medium. Fibres located at the edge of the eutectic cells had an average length of up to $100\ \mu\text{m}$ (Fig. 3), whereas fibres found inside pits in the inter-cellular space were generally not longer than $10\ \mu\text{m}$ (Fig. 4). The fibres observed in the inner areas of the cells were normally parallel to each other,

Table 1
Metal contents obtained by ICP-OES after treatment of the NiAl–Re alloy with HCl:H₂O₂

Sample	Metal content					
	Al		Ni		Re	
	mg/l	% (w/w)	mg/l	% (w/w)	mg/l	% w/w
NiAl–Re alloy	–	29.9	–	65.0	–	5.5
Filtered solution ^a	6780	31.2	14550	66.9	420	1.9
Filtration membrane ^a	0.22	–	0.24	–	~ 0.01	–

^a Recovered after filtration of the alloy sample treated with HCl:H₂O₂.

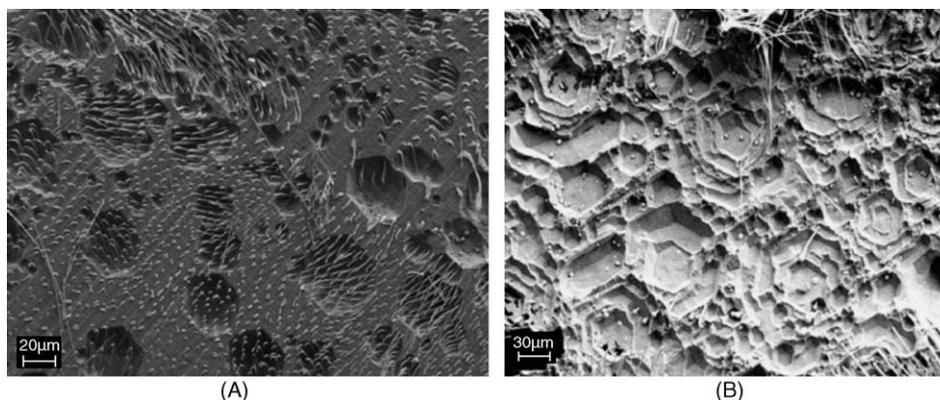


Fig. 2. Anisotropic etching observed in a NiAl–Re alloy after digestion in a 3.2% HCl, 3% H₂O₂ mixture for 4 h.

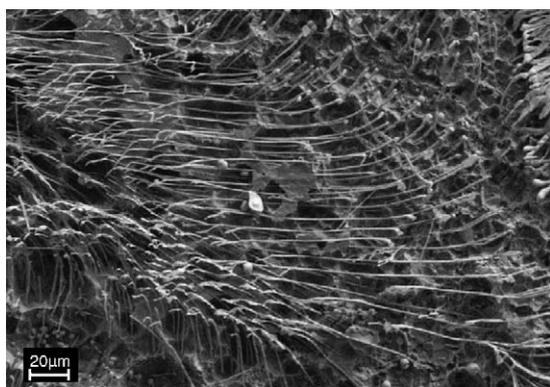


Fig. 3. Long rhenium fibres observed at the edge of eutectic cells after 4 h digestion in a mixture of 3.2% HCl and 3% H₂O₂.

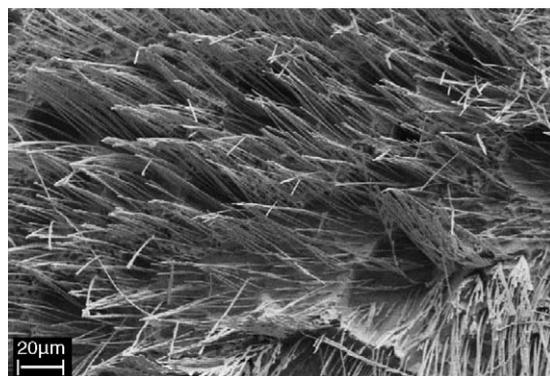


Fig. 5. Rhenium fibres distributed inside eutectic cells after digestion of a sample in 3.2% HCl and 3% H₂O₂ for 30 min.

and showed almost identical features. The digestion time was also found to play a significant role on the formation of fibres, although well-defined, long nanowires were observed after only 30 min (Fig. 5). Long digestion times also resulted in a severe corrosion, which produced deep pits into which the fibres were dug—the deeper the pit, the larger the fragment of fibre visible through the structure (Fig. 6). The composition of the obtained structures was confirmed by energy-dispersive X ray (EDX) and found to be exclusively rhenium (Fig. 7).

The production of rhenium nanowires by selective etching also helped to determine their crystallographic nature. In an early work on single-phase materials, Jackson distinguished between “non-faceted” phases that solidify with complete crystallographic isotropy via an atomically rough solid/liquid interface, and “faceted” phases that have preferential crystallographic growth directions associated with atomically smooth solid/liquid surface facets [12]. The presence of fibres with rectangular shape, which are constrained

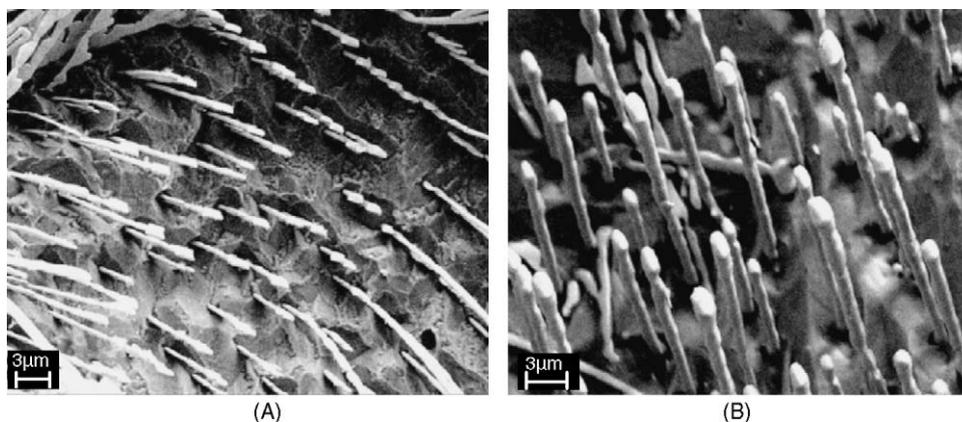


Fig. 4. Short rhenium fibres observed after digestion of eutectic samples in 3.2% HCl and 3% H₂O₂ for (A) 30 min, and (B) 8 h.

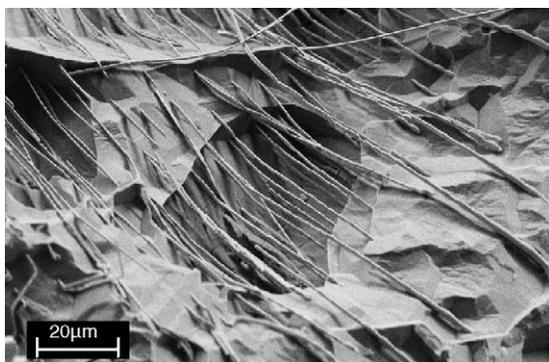


Fig. 6. Rhenium fibres embedded in pits created in the NiAl matrix by 3.2% HCl and 3% H₂O₂ (digestion time 8 h).

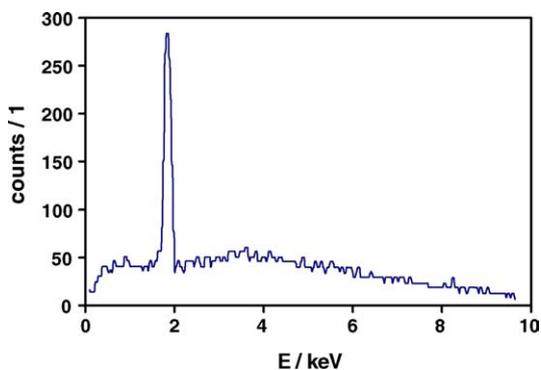


Fig. 7. EDX spectrum recorded for rhenium fibres.

with two perpendicular crystallographic directions (Fig. 8), suggests the faceted nature of the rhenium phase.

3.2. Digestion of the NiAl–Re eutectic in 5 M H₂SO₄

Immersion of eutectic samples in 5 M H₂SO₄ only produced a significant etching of the matrix after long digestion times (>8 h), mainly due to the lower oxidising strength of the solution. A few disperse short fibres were found on the surface for digestion times between 1 and 8 h, whereas exposure of the sample for 24 h resulted in well defined rhenium

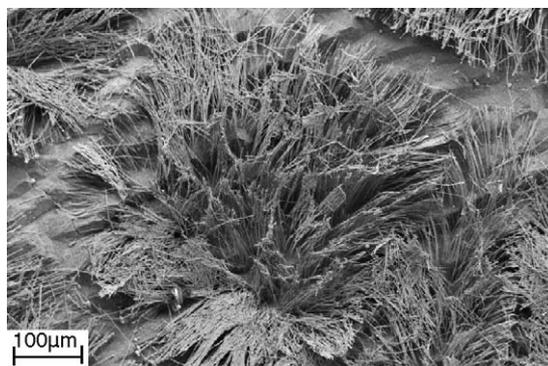


Fig. 9. Distribution of rhenium fibres inside eutectic cells after etching of samples with 5 M H₂SO₄ for 24 h.

fibres, with similar lengths and patterns, and organised within the eutectic cells (Fig. 9). These cells were clearly visible and defined after removal of the matrix, with the inter-cells space showing preferential etching directions (Fig. 10), yielding a structure similar to a staircase with fibres agglomerates on either side. The composition of the obtained fibres was also determined as pure Re by EDX analysis.

Dissolution of all three elements (Ni, Al, and Re) was observed after treatment of the sample in aqua regia (HNO₃:HCl, 1:3). The oxidising power is obviously high enough for both phases and all elements. Thus, the so obtained solution was employed to confirm the overall composition of the alloy and the samples used.

4. Discussion

The selective dissolution of the matrix from a NiAl–Re eutectic was feasible after digestion of the sample in solutions with different oxidising powers. Thus, the use of 5 M sulphuric acid only yielded the desired etching after long exposure times (>8 h), whereas the use of a mixture of diluted HCl:H₂O₂ displayed a higher oxidising power and produced a significant etching of the matrix after immersion times as

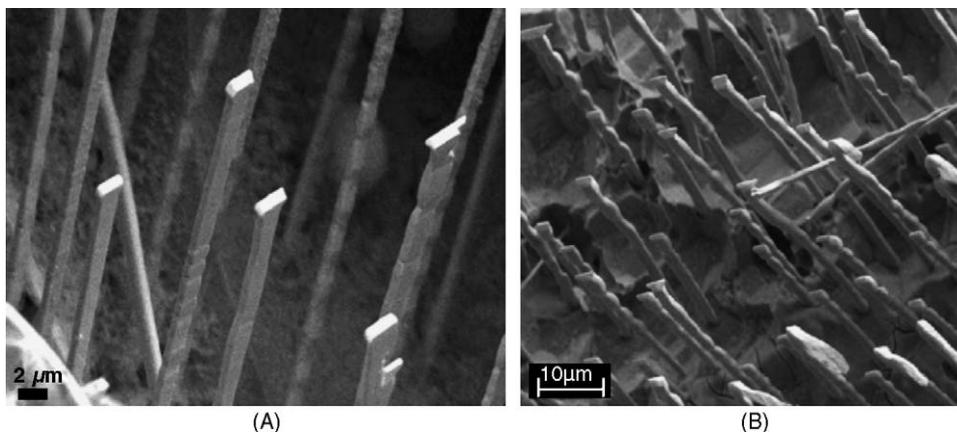


Fig. 8. Faceted rhenium fibres found in samples digested in 3.2% HCl and 3% H₂O₂ for 6 h.

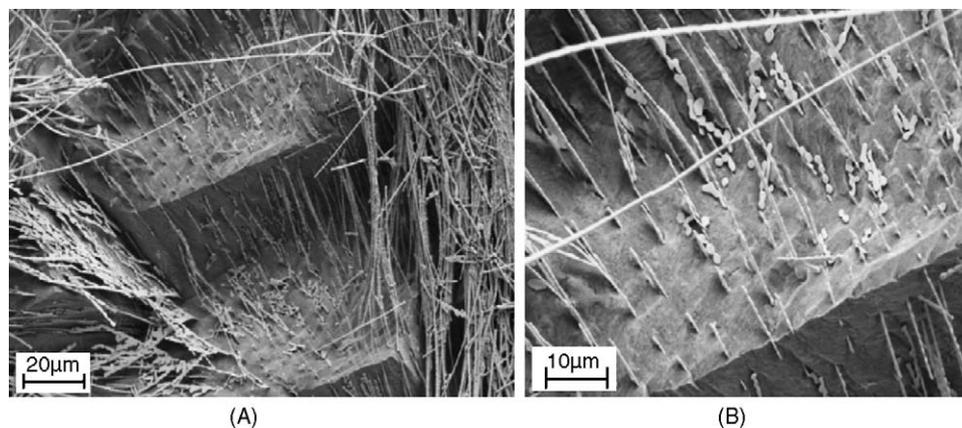


Fig. 10. Anisotropy observed in the etching of NiAl-Re samples with 5 M H₂SO₄ for 24 h.

short as 30 min. The oxidising nature of the H₂O₂, combined with the extensive pitting corrosion originated by the HCl, favoured the dissolution of the matrix when compared to H₂SO₄. Total dissolution of the alloy was observed in aqua regia, as used for ICP-OES analysis.

The open circuit potential of each of the alloy phases (namely Re and NiAl), showed values close to 0 V for NiAl in all three investigated solutions (HCl:H₂O₂, 5 M H₂SO₄ and aqua regia), which is the potential range kept in the experimental conditions investigated during this work. Re, on the other hand, presented a higher corrosion potential for each of the studied solutions (Table 2), and thus its oxidation is hindered without the application of an external voltage. The NiAl phase is therefore dissolved into the solution, whereas rhenium stays unaltered. The highest corrosion potential for pure rhenium was placed at 0.82 V in a HCl:H₂O₂ mixture, compared to a much lower 0.49 V in 5 M sulphuric acid. Dissolution of rhenium would therefore be more favoured when the latter is employed. The high value registered for the corrosion potential of rhenium in aqua regia may be explained by partial passivation of the metal in the concentrated acidic solution. Needless to say, the high oxidation power of this solution yielded the complete dissolution of all three elements, compared to the immunity observed for rhenium in HCl:H₂O₂ or H₂SO₄ at the studied times.

The regular patterns found in the inter-cellular spaces in the matrix after digestion with either solution suggest an anisotropic etching of the NiAl phase, with preferential etching orientations. Electron back scatter diffraction (EBSD) analysis of the NiAl–Re eutectic showed a $\langle 100 \rangle$ crystallographic orientation of the growth direction for the NiAl

matrix. The presumption of a preferential direction in the oxidation process was enforced by the parallel structures observed after etching. The rough surface of the attacked sample restrains any EBSD analysis, and thus alternative methods must be considered in order to investigate this possibility further.

The presence of long fibres at the edge of the eutectic cells was a common observation for all the investigated digestion times. SEM analysis of eutectic samples prior to their exposure to any etching solution showed eutectic cells evenly distributed on the alloy surface. The rhenium fibres could be visibly distinguished from the matrix, as they appeared as independent dots placed in parallel along the cells. However, it was also observed that such rhenium structures were more irregular on the edges, with a higher presence of long specimens than dots (Fig. 11). Etching of the sample would just free such structures, resulting in the formation of long rhenium fibres, as observed experimentally. Etching of the matrix within the inner space of the cells gave a final structure dominated by arrays of parallel fibres (constrained within the cellular space). However, fibres with different lengths and features were observed in other sections of the sample. These differences in shape may be the result of a lower exposure to the attacking solution. Long digestion times may result in an increase in the corrosion potential, which would then

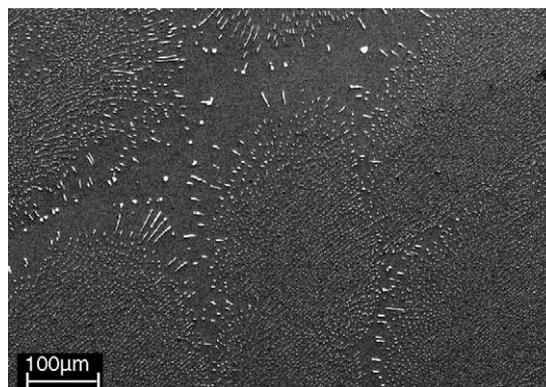


Fig. 11. SEM image of a NiAl–Re eutectic prior to chemical etching.

Table 2

Free corrosion potential measured for each of the eutectic phases (NiAl and Re) in the investigated etching solutions (potential values given vs. SHE)

Etching solution	Component	
	E_{Re}/V (SHE)	E_{NiAl}/V (SHE)
3.2% HCl:3% H ₂ O ₂	0.825	0.043
5 M H ₂ SO ₄	0.498	−0.03
HCl _{conc} :HNO _{3conc}	0.700	−0.09

favour the dissolution of some of the rhenium. This effect would result in smaller fibres, as observed in certain cases. The smallest rhenium structures were often found outside the defined eutectic cells, with a shape closer to a sphere than a fibre. These structures may result from the presence of rhenium in the NiAl matrix from the solidifying process. The region at the rim of a eutectic cell has a composition different from the eutectic composition. Thus, the directional solidification cannot produce material of the same degree of order as within the cells.

5. Conclusions

Fabrication of Re nanowires has been achieved by selective etching of the matrix in eutectic alloys. The obtained rhenium nanofibres showed patterns influenced by the exposure to the investigated solutions, which was mainly determined by their initial position in the alloy and/or digestion time. The overall structure of the matrix and the fibres embedded in it was also found to be determined by the oxidising solution employed. The fabricated fibres can later be used as nanosensors array after appropriate insulation of the inter-space left after corrosion of the matrix. The use of the refractory metal rhenium as nanoelectrode can be exploited for its use in high-temperature measurements. An alternative route for the fabrication of nanostructures from eutectic alloys has previously been investigated by passivation of the matrix in neutral acetate buffer and dissolution of the rhenium fibres [11]. The produced nanopores can subsequently be filled with noble metals (platinum, gold), for the fabrication of Au or Pt nanosensors.

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