

A novel concept for the preparation of alloy nanowires

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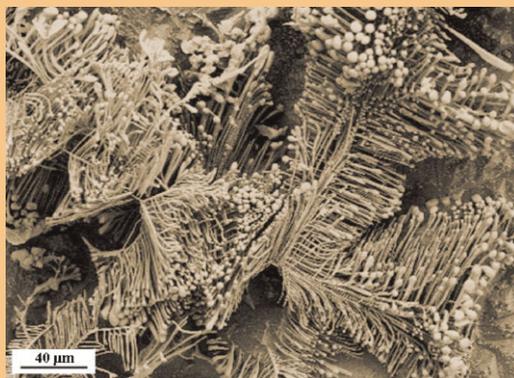
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A novel concept for the preparation of alloy nanowires has been developed. By combining two pseudobinary eutectic systems NiAl–W and NiAl–Cr with a completely miscible system Cr–W, a pseudoternary system was created in which there is large two-phase field between NiAl and W(Cr) solid solutions, separated by a eutectic trough. This enables the fabrication of nanowires with compositions from pure W to pure Cr allowing a free change of the ratio. The directional solidification in the pseudoternary system has been carried out. For the first time alloy nanowires in the W–Cr system have been reported. In addition, nanowires of pure W and Cr were fabricated as well. Moreover, an electrochemical procedure for the release of nanowires from the matrix has been established.



High yield of W–Cr alloy nanowires with equiatomic composition.

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1 Introduction Various methods have been developed to fabricate tungsten nanowires. Thong et al. [1] obtained single tungsten nanowires by field-emission induced growth in the presence of tungsten carbonyl as a precursor. Nanowires have been grown on carbon nanotubes [2], AFM tips [3] and between two microtip electrodes [4]. Li et al. [5] used pyrolysis and carbothermal reduction of lamellar composites of tungsten oxide with cetyltrimethylammonium bromide (CTAB) in vacuum between 500 and 850 °C to produce metallic W nanowires with diameters in the range of 20–80 nm and lengths 5–30 μm. Hydrothermal treatment of lamellar structures also yielded crystalline metal nanowires [6]. Liu et al. [7, 8] investigated features and growth behaviour of self-supporting tungsten nanowires fabricated by electron-beam-induced deposition using 200 keV electrons. Wang synthesized single-crystalline tungsten nanowires by a nickel-catalysed vapour-phase method controlled by a vapour–solid–solid mechanism [9].

Also, Lee et al. [10] reported on the field emission properties of nanosized straight tungsten wires fabricated by annealing of a W film which behaves as a self-catalytic layer. Finally, Ross fabricated amorphous tungsten nanowires by electron and ion beam induced chemical vapour deposition (CVD) [11].

Regarding chromium nanowires the number of studies is much lower. Lee et al. [12] reported on the direct lateral growth method of Cr nanowires based on the one-step autocatalytic function of the Cr. Shim synthesized highly crystalline Cr nanowires on a flexible polymeric substrate using microwaves [13]. In addition, Lee et al. [14] applied direct metal transfer (DMT) using a two-step thermal treatment to transfer Cr wires at 70 nm half-pitch to an organic active layer. Further, by using nanoimprint lithography Lee et al. [15] fabricated a 70 nm narrow Cr nanowire structure on a flexible PET film. After brief oxygen plasma treatment and e-beam evaporation of Cr, resist patterns were

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lifted-off with acetone solution, thus forming a uniform Cr nanowire structure on a flexible PET substrate.

Alloy nanowires have been mostly synthesized by electrodeposition of metals in an anodized alumina oxide (AAO) template. To name just a few, the alloy nanowires in the following systems have been reported: Co–Sn [16], Co–Ni [17, 18], Fe–Pd [19], Co–Pt and Fe–Pt [20]. Another system that has been extensively studied is the Si–Ge system. The effect of various process conditions on the composition of $\text{Si}_{1-x}\text{Ge}_x$ nanowires has been investigated using various synthetic techniques, such as laser-assisted catalytic growth (LCG) [21], CVD [22], molecular beam epitaxy (MBE) [23] and vapour–liquid–solid (VLS) method [24, 25]. It has been shown that by the latter method $\text{Si}_{1-x}\text{Ge}_x$ nanowires can be grown in the entire composition range by controlling the $\text{GeH}_4/(\text{GeH}_4 + \text{SiH}_4)$ inlet gas flow ratio and the growth temperature.

Beside the above mentioned methods, there have been also several innovative attempts. For instance, Fedutik [26] synthesized nanowires of Co–Ni and Fe–Ni in an applied magnetic field via chemical reduction with Ti(III) in aqueous solutions. In addition, Liu et al. [27] established a novel synthesis of ultra thin CoPt_3 nanowires by dealloying larger diameter $\text{Co}_{99}\text{Pt}_1$ nanowires and subsequent stress-induced crack propagation. However, to the best of authors' knowledge no fabrication method of the alloy nanowires in the Cr–W system has been reported so far.

2 Experiments

2.1 Sample preparation The prealloys of all samples were produced through induction melting of the metal powders and casting in a water-cooled copper mould. Afterwards the samples were directionally solidified in a Bridgman furnace with a pulling rate of 30 mm h^{-1} and a temperature gradient of 40 K cm^{-1} for all the samples. The composition of the NiAl–Cr alloys used was 34 at.% Cr with an equiatomic ratio of Ni and Al. In Table 1 the composition of the used pseudobinary NiAl–CrW alloys is given. The samples were cut into 1 mm slices, mechanically ground to remove the oxide scale and subsequently cleaned through ultrasonication in ethanol.

2.2 Solutions and procedures Based on the combined Pourbaix diagrams of the respective metals, conditions for the selective electrochemical dissolution of the desired elements while keeping others passive or, respectively, immune, can be chosen. To dissolve the NiAl matrix of the samples two different types of solutions were used. For the initial electrochemical experiments on NiAl–Cr 1 M HCl

was utilized. Based on this concept additionally a solution containing 20 ml HCl, 5 g CrO_3 (0.36 mol L^{-1}) and 100 ml distilled water was prepared.

All solutions were prepared using hydrochloric acid (32%, Merck). The electrochemical dissolution of the matrix of NiAl–Cr was performed in 1 M HCl at a potential of 200 mV (SHE) using a Potentiostat (1286 Electrochemical Interface Solartron Analytical). Further digestion of both NiAl–CrW and of NiAl–Cr was only carried out chemically under addition of CrO_3 . After completing the etching process an ultrafiltration system (Sartorius) with cellulose acetate filter paper (pore size 200 nm) was utilized to collect nanowires from the etching solutions used.

3 Results and discussion

3.1 Alloying concept A phase diagram is a graphical representation of chemical equilibrium. Since chemical equilibrium is dependent on the composition of the system, the pressure and the temperature, a phase diagram shows which phases are in equilibrium for a given composition at a certain temperature and pressure of the system.

The Gibbs phase rule is an expression of the number of variables and equations that can be used to describe a system in equilibrium. In simple terms, the number of variables is the number of chemical components in the system plus the intensive variables, temperature and pressure. The number of phases present will depend on the variance or degrees of freedom of the system. The general form of the phase rule is stated as follows:

$$F = C + 2 - P, \quad (1)$$

where F is the number of degrees of freedom or variance of the system, C the number of components, P the number of phases in equilibrium and the integer 2 is the number of intensive parameter variables, pressure and temperature. For the system with constant pressure the Gibbs phase rule is:

$$F = C + 1 - P. \quad (2)$$

A eutectic transformation is a reaction in which a liquid phase (melt) transforms into two solid phases:



At the eutectic point in a two component system, all three phases, that is liquid, crystals of α and β , all exist in equilibrium. The eutectic point is the only point in the diagram where this is true. Applying the Gibbs phase rule, it follows that for the binary (two component) system at the eutectic point where three phases are in equilibrium the degree of freedom is 0. This means that the temperature must remain constant until one of the phases disappears, which makes the eutectic transformation an invariant reaction.

The directional solidification of eutectic alloys under controlled growth conditions generally yields lamellar or fibrous structures, aligned parallel to the direction of heat extraction, i.e. the growth direction. Recently, it has been demonstrated that the combination of directional

Table 1 Composition of the eutectic NiAl–CrW alloys in at.%.

W/Cr (at.%)	Cr at.%	W at.%	Ni at.%	Al at.%
75:25	0.5	1.5	49.0	49.0
50:50	1.5	1.5	48.5	48.5
25:75	4.2	1.4	47.2	47.2

solidification of eutectic alloys with fibre morphology and posterior selective dissolution of the matrix is a novel and successful tool for the fabrication of nanowire arrays [28]. This method surpasses several drawbacks of other available techniques for the fabrication of metallic nanostructures. Firstly, no template or seed is necessary as it is based on self-organization of metallic phases through a diffusion controlled growth. Additionally, both nanowires and matrix are single crystalline which may favour them for certain applications. Moreover, the obtained nanostructures exhibit extremely high aspect ratios (>1000), unreachable by most of the techniques. Finally, the method is highly versatile and applicable to a broad range of materials for different applications. It has been successfully employed for the fabrication of Re [29, 30], W [31, 32], Mo [33, 34], Cu [35] nanowires and Au nanobelts [36–39].

The classical theory of eutectic growth was proposed by Hunt and Jackson [40] in mid 1960s. They assumed a maximum of the growth velocity, and obtained the following relationship between growth rate V and the inter-phase spacing λ , for both lamellar and fibrous eutectic structures:

$$\lambda^2 V = K_1. \quad (4)$$

It has been shown that the wire diameter and spacing can be controlled by the processing parameters such as growth rate and temperature gradient according to the above relationship [41]. It should be noted, that the solidification rate cannot be used to vary the inter-phase spacing without limit because the growth mechanism forming well-aligned microstructures breaks down at very low and very high

growth rates, being replaced with the so-called degenerated and cellular structures, respectively [42, 43]. Change in the wire spacing leads to change in the wire diameter and density *vice versa*. However, they cannot be changed independently because the volume fraction of the phases, defined by the eutectic point is fixed. In order to circumvent this drawback the following approach is suggested. The basic idea is to extend the binary system into a ternary, so that an additional degree of freedom is gained. This can be achieved by combining two simple binary eutectic systems with a binary system with complete miscibility. An example is the pseudo ternary NiAl–Cr–W system. The NiAl–W pseudobinary subsystem is a simple eutectic with eutectic point at 1.5% W and 1664 °C [44]. Similarly, NiAl forms a eutectic with Cr at 1490 °C and 34 at.% Cr [45]. The third binary subsystem is the Cr–W with complete solubility [46]. In the case of three binary eutectic subsystems, the ternary system would present a ternary eutectic. As in the above case, the third binary subsystem is a system with complete miscibility, instead of ternary eutectic, the ternary system will comprise eutectic trough between two ending binary eutectics. In the presented case, it means that there exists a eutectic trough between NiAl–1.5% W and NiAl–34% Cr. This practically means that changing the ratio of Cr and W along the eutectic trough it is possible to change the volume fraction of the minor W(Cr) phase. As W and Cr are completely miscible and have the same crystal structure (BCC) it implies that the fibrous eutectic phase will only change in composition. The pseudoternary NiAl–Cr–W, the two pseudobinaries NiAl–Cr and NiAl–W, as well as the binary Cr–W subsystem are shown in Fig. 1. The region of interest is zoomed in Fig. 1b.

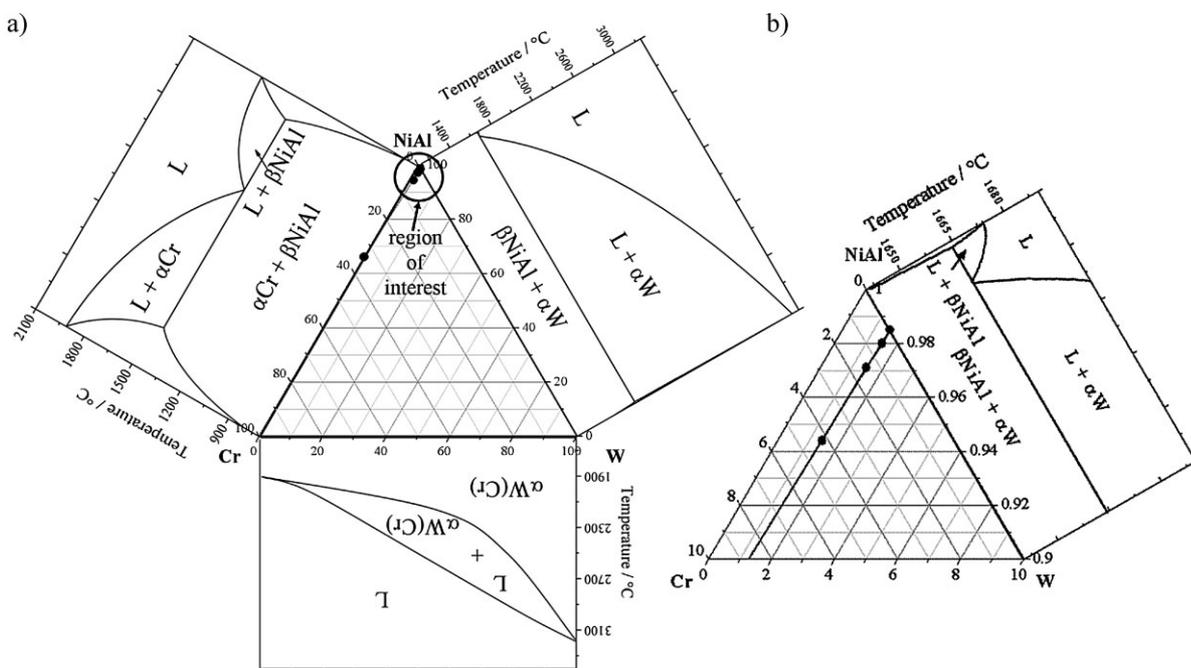


Figure 1 (a) Pseudoternary NiAl–W–Cr phase diagram with binary subsystems and (b) magnified region of interest with the compositions of investigated alloys.

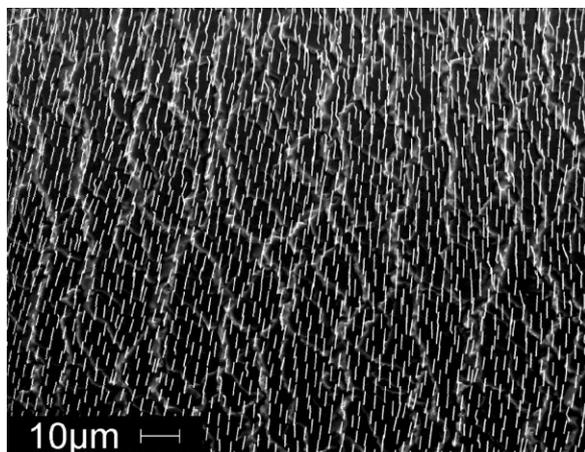


Figure 2 Array of W nanowires.

Thus, in the region of eutectic trough, a range of pseudobinary eutectics between NiAl matrix and solid solution of W and Cr denoted W(Cr) exists, where the volume fraction can be changed between 1.5 and 26%.

Another important aspect of the suggested concept is that it allows fabrication of alloy nanowires with continuous change in composition from 100% W to 100% Cr. The feasibility of the concept has been proven by preparing the alloys with compositions listed in Table 1 and depicted in the ternary diagram in Fig. 1b. The compositions have been chosen in such a way that the ratio of W/Cr is 75:25, 50:50 and 25:75, respectively.

3.2 W nanowires Fabrication of W nanowires by directional solidification and electrochemical processing of NiAl–W eutectic alloys has been successfully performed. Initially, the conditions for the nanowire release have been determined [31]. Both, the nanowire arrays and loose nanowires were obtained, as exemplified in Fig. 2.

Additionally, process parameters have been optimized to control the spatial features of the nanowires namely spacing, diameter and density [47]. Furthermore, the extracted wires were used to build nanoelectromechanical system (NEMS) and study their mechanical properties [48]. Finally, it has been demonstrated that large scale synthesis in the laboratory conditions is feasible. The amount of 1 g of W nanowires, corresponding to approximately 5 billions of nanowires has been produced [49].

3.3 Cr nanowires In order to find the right conditions for the production of CrW-nanowires, initial experiments on NiAl–Cr are necessary to test the transferability of the approved etching conditions of the NiAl–W system to a new quaternary system. Therefore the conditions applied to the NiAl–W system are adapted to the NiAl–Cr system. Figure 3 shows the SEM micrograph of a NiAl–Cr sample which was electrochemically etched in 1 M hydrochloric acid at a potential of 200 mV (SHE) for 30 min. The formation of porous structures points out the higher dissolution rate of

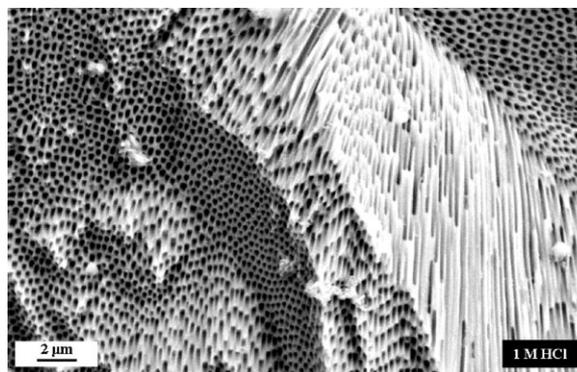


Figure 3 NiAl–Cr partially etched in 1 M HCl.

chromium. Although it could be proven by inductively coupled plasma optical emission spectrometry (ICP-OES) measurements that both nickel and aluminium are dissolving in equimolar amounts the amount of chromium dissolved in the solution is thrice. ICP-OES measurements were performed using a Thermo Iris Intrepid Duo HR from Thermo Fisher Scientific.

In compliance with the combined Pourbaix diagram of the quaternary system, shown in Fig. 4, appropriate conditions to actively dissolve both nickel and aluminium can be found in the pH-region above pH=13.0 or in the acidic region. To circumvent using highly alkaline solutions, a solution mainly based on the previously applied hydrochloric acid system was used. According to Cline and Walter [50, 51] who examined growth phenomena and structures of NiAl–Cr eutectics a solution containing $0.36 \text{ mol L}^{-1} \text{ CrO}_3$ was prepared. As shown in Fig. 5 structures of aligned nanowires are already visible after an etching duration of 1 min.

3.4 Alloy nanowires Transferring the conditions applied for the NiAl–Cr system to the pseudoternary system,

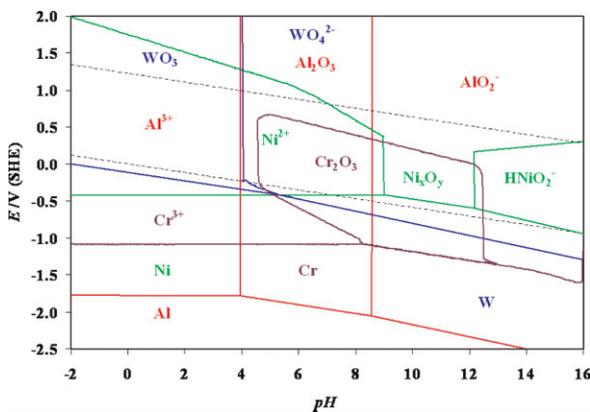


Figure 4 (online colour at: www.pss-a.com) Combined Pourbaix-Diagram of Ni, Al, Cr and W (adapted from Ref. [52]). By means of clarity only lines for a concentration of the dissolved species of $10^{-6} \text{ mol L}^{-1}$ are given.

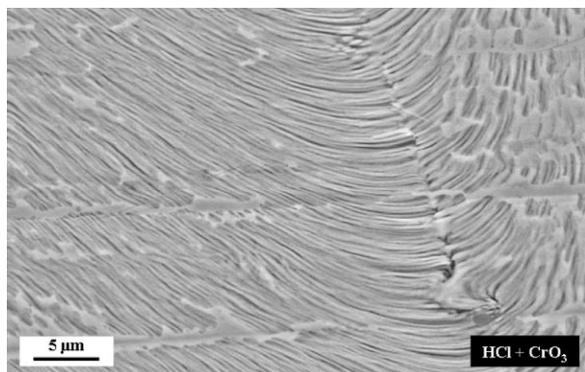


Figure 5 NiAl–Cr sample partially etched in a hydrochloric acid solution containing $0.36 \text{ mol L}^{-1} \text{ CrO}_3$.

samples of three different compositions, listed in Table 1, were digested for 15 h in the aforementioned solution containing both hydrochloric acid and chromium(VI)oxide.

The partial dissolution of the samples allowed, combined with the usage of an ultrafiltration system, obtaining both loose wires dispersed on a silicon wafer and wires embedded in the matrix.

SEM micrographs, as shown in Fig. 6, depicted especially for a nominal equiatomic ratio of W and Cr a large number of nanowires with a high aspect ratio. The average diameter of wires of all compositions was determined to be 600 nm. The composition of the wires was analysed using energy dispersive X-ray spectroscopy (EDS) measurement of the embedded wires which displayed for the sample with an expected W/Cr ratio of 50:50 a content of 56 at.% W. This shift against the theoretical composition might be a result of the selective dealloying during chemical treatment in which chromium is dissolved at the surface and tungsten is enriched on the surface of the nanowires. A similar small difference in the compositions was found for the other two alloys. Additionally, ICP analysis of the etching solutions showed again equiatomic amounts of both W and Cr in solution. Thus, through these individual methods the selectiveness of the dissolution process was verified.



Figure 6 WCr (50:50) alloy nanowires partially showing growth irregularities and branched structures.

According to the combined Pourbaix diagram shown in Fig. 4, at the calculated pH of the solution of -0.5 , chromium should dissolve as Cr^{3+} in addition to the dissolving matrix elements. Hence, the Pourbaix diagram does not give a direct explanation for the solely dissolution of the matrix elements. An addition of CrO_3 leads to the formation of chromic acid which reacts in acidic solutions to form Cr^{3+} as shown below:



Also the line confining the region of immunity of Cr is slightly shifted to higher potentials.

This alone could not explain the apparent immunity of chromium to the selective dissolution. A supplementary effect of this addition is the creation of highly oxidizing conditions which results in a preferential formation of WO_3 . As a result Ni and Al dissolve continuously and an inaugural amount of Cr may be dissolved. Actually, chromium is dissolved only at the surface of the nanostructures, while due to the highly oxidizing conditions released metallic W is transformed into WO_3 which is covering the nanowires protecting the structures from further dissolution. Olsson and Landolt [53] previously discussed similar effects in stainless steels using the percolation theory. It is based on the 1/8 concept, stating that for a system with BCC structure, such as the iron–chromium system, when the content of Cr is higher than 1/8 (12.5 at.%) 50% of the Cr atoms have a minimum of one Cr atom as nearest neighbour. Thus, a continuous network of Cr atoms in the bulk material is formed. The gap between these atoms can be bridged by a hydroxide or oxide chain passivating the surface of a material which was already shown by Newman et al. [54]. So, applying the percolation theory to our case, the content of W is more than sufficient to form a continuous network of atoms, bridged by an oxide chain and thus forming a passive layer on the nanowire surface, protecting them from further dissolution. Indeed, in a previous study on the W nanowires, it has been demonstrated that these are covered by a thin oxide layer of approximately 6 nm in thickness [49].

4 Summary For the first time alloy nanowires in the W–Cr system have been reported. Alloy nanowires with different compositions were synthesized. A novel concept for the preparation of alloy nanowires has proven to be feasible. By combining two pseudobinary eutectic systems NiAl–W and NiAl–Cr with a completely miscible system Cr–W, a pseudoternary system was created in which there is a large two-phase field between NiAl and W(Cr) solid solutions separated by a eutectic trough. This enabled the fabrication of nanowires with compositions ranging from pure W to pure Cr changing freely their ratio. In addition, the nanowires of pure W and Cr were fabricated as well. Moreover, an electrochemical procedure for the release of nanowires from the matrix has been established.

Both W and Cr are refractive metals and possible applications may be seen in the emerging field of high

temperature nanotechnology. With respect to the high price of W it can be interesting to tune properties and effective price into an optimum.

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