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Electron microscopy and electron diffraction study of ordering in Ni_4W

The intermediate phase Ni_4W in the nickel–tungsten system undergoes an order–disorder transformation at 970 ± 10° C. The disordered phase is f c c while the ordered phase is b c t with $c/a = 0.980$. Extensive electron microscopic and field-ion microscopic investigations have been carried out on the nature of ordering and the transformation from short range order (SRO) to long range order (LRO) in the structurally similar Ni_4Mo [1–6], but only one X-ray analysis [7] and one field-ion microscopic investigation on growth of Ni_4W from the disordered phase is reported in the literature [8]. The present communication reports some transmission electron microscopic observations of SRO and the development of LRO in Ni_4W.

Samples were taken in the form of thin sheets,

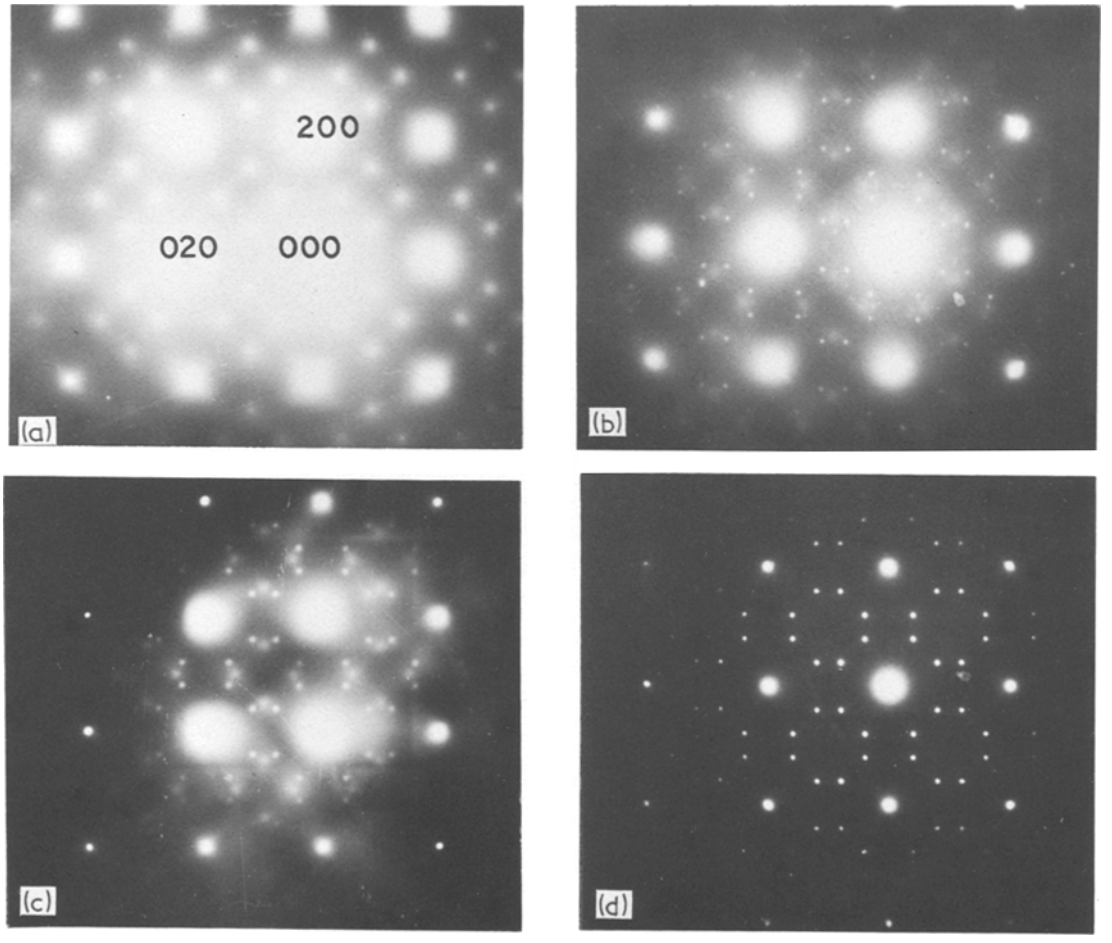

Figure 1 Electron diffraction patterns corresponding to the $[0\,0\,1]^*$ reciprocal lattice section of Ni_4W quenched from 1125° C and aged at 830° C for (a) 0 min (b) 15 min (c) 20 min (d) 30 min.

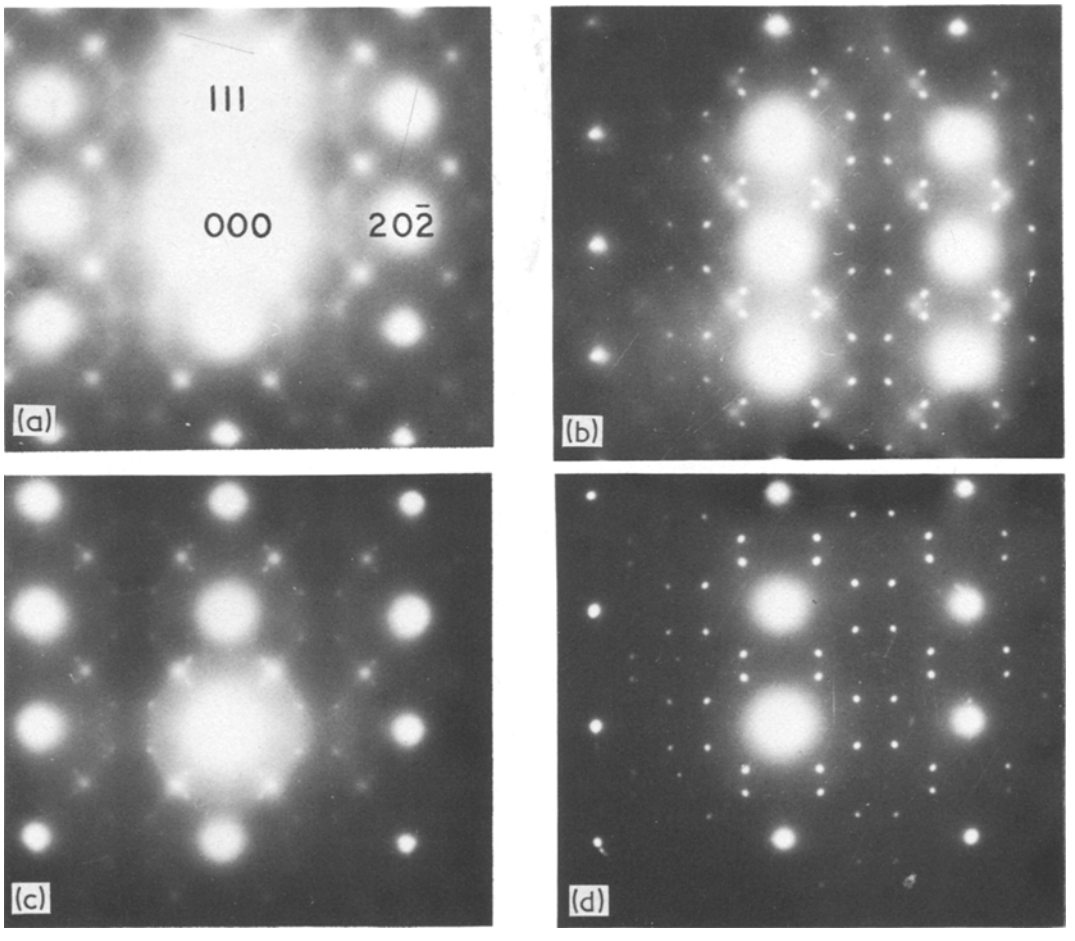

Figure 2 Diffraction patterns corresponding to the $[1\,\bar{2}\,1]_{fcc}$ reciprocal lattice section of the Ni_4W alloy for the same annealing times as in Fig. 1.

disordered for 4 h at 1125°C and quenched in water. The as-quenched material was then annealed at 830 or 940°C for different times between 5 min and 200 h. Samples suitable for electron microscopy were electro-polished in a solution containing 4 parts hydrofluoric acid, 2 parts concentrated sulphuric acid, 2 parts concentrated phosphoric acid and 1 part concentrated glacial acetic acid in 75% water.

Electron diffraction patterns of $[0\,0\,1]^*$ and $[1\,\bar{2}\,1]^*$ sections are shown in Figs. 1 and 2 respectively. The different alloys are annealed for 0, 15, 20 and 30 min at 830°C. This temperature was chosen as the optimum based on the earlier work of Tong and Washburn [8]. In the as-quenched state diffuse intensity maxima appear at different $\{1\,\frac{1}{2}\,0\}$ positions, indicating the presence of SRO. The form of the SRO spots is spherical and very similar to the ones observed in Ni_4Mo. Apart from the $\{1\,\frac{1}{2}\,0\}$ reflections supplementary diffuse intensity is observed in between different SRO spots; this is clear from the $[1\,\bar{2}\,1]^*$ section where diffuse streaking is observed not only in the $[4\,2\,0]^*$ and the $[0\,2\,4]^*$ directions but also along other directions. The presence of this intensity and the investigation of different reciprocal lattice sections strongly suggests an initial ordering accompanied by cluster formation, but different from the one observed in Ni_4Mo [4]. Dark-field microscopy of $\{1\,\frac{1}{2}\,0\}$ reflections reveals the presence of micro-domains of the order of 30 Å (Fig. 3). Similar domains are reported on field-ion microscopic investigations by Tong and Washburn [8].

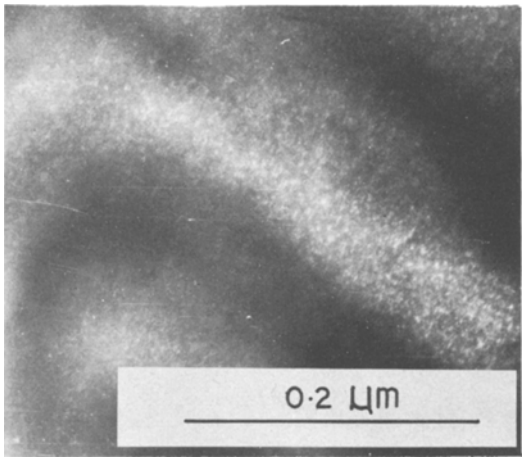

Figure 3 Dark-field electron micrograph in a $(1\frac{1}{2}0)$ reflection showing the presence of microdomains.

On ageing for 5 to 10 min at 830° C diffuse intensity remains and after only 15 min do intensity maxima appear around the Ni_4W superlattice positions (Figs. 1b and 2b). SRO and LRO co-exist after 20 min (Figs. 1c and 2c) and on annealing for 30 min SRO disappears completely. At this stage dark-field micrographs show a homogeneous distribution of ordered particles of about 500 Å size (Fig. 4a). On ageing for 200 h at 940° C or 830° C these domains grow to about 1 μm (Fig. 4b). It is to be noted that the direction of growth in this case is $\langle 1\,1\,0\rangle_{fcc}$, in agreement with earlier observations [9].

From the above observations it can be concluded that the ordering sequence in Ni_4W although slightly different, is similar to the ordering in Ni_4Mo. Ordering proceeds homogeneously and the habit plane for domain growth is found to be $\{1\,1\,0\}_{fcc}$.

A detailed study of the exact form and the interpretation of diffuse intensity due to the transition from SRO to LRO is in progress and will be reported later.

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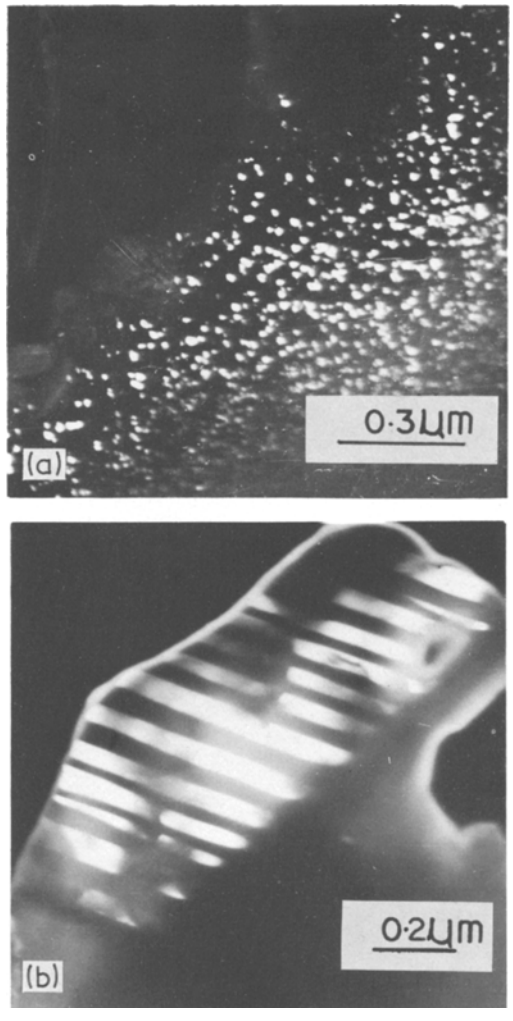

Figure 4 Dark-field electron micrographs in a Ni_4W superlattice reflection after annealing for (a) 30 min at 830° C and (b) 200 h at 940° C. Note the presence of twin boundaries along the $(1\,1\,0)_{fcc}$ planes.

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$Nb_6(GaAs)$, $Nb_6(InSb)$ and $Nb_6(GaP)$ new "half-breed" ternary superconductors

While there is, as yet, no basic understanding of the relation of structure or composition to the superconducting transition temperature, empirical search has led to the dominance of two structures: NaCl and β-W, and many compositions involving the element Nb. The discovery that "Nb_3Ge" thin films could be prepared with T_c as high as 22.7 and 23.1 K was a step function advance in this empirical approach. We describe herein a logical extension of this search by the application of elementary crystal chemical principles. The principal aim is to obtain a slight change in band structure of the β-W phase by total elemental substitution. Since the work of Goldschmidt [1] the principle of "half-breeding" to place new elements into a selected structure has been well known. Thus $Si^{4+}O_2$ with the quartz and cristobalite structures can be "half-bred" by replacing Si^{4+} by $(Al^{3+} + As^{5+})$ or $(Ga^{3+} + p^{5+})$ etc. The properties of the resulting $AlAsO_4$ or $GaPO_4$ phases are useful and interesting variants of the properties SiO_2 [2, 3]. The whole families of III-V and II-VI semiconductors are, of course, also based on this reasoning (thus [1] p. 144 listed, in 1926, all known useful half-breed III-V and II-V; semiconductors). The present study reports preliminary results on attempting to make [β-tungsten] phases based on Nb_3Ge, with Ge replaced by GaP, AlAs, InSb, and AlSb.

Two approaches were taken to prepare the ternary compounds. The first was an attempt to prepare ingots by solid state reaction at low temperatures. The second was by sputtering onto hot and room temperature substrates. Films deposited on the room temperature substrates were later annealed. For the former, weighed and thoroughly mixed powders were heated in sealed silica tubes for 75 h over a range of temperatures. For the r.f. sputtering, the general methods developed in this laboratory [4] were used. Small single crystal sections (roughly 2 cm^2) of the III-V compound were cemented, off-centre, on a niobium target. This permits one to obtain a range of compositions in one run. Although polished polycrystalline Al_2O_3 and silica glass were used in the overall study, the results presented are principally from the films laid down on polycrystalline Al_2O_3. Some twenty films are made in each run. The films so prepared have been analysed routinely with respect to composition on the electron probe, and structure by X-ray diffractometry.

T_c has been measured on the films utilizing a very simple apparatus [5]. In several cases John Gavaler has kindly also measured the samples at the Westinghouse Research Laboratories.

The results of the solid state reacted ingots were immediately of interest, since three obviously isostructural phases were obtained. However, the powder X-ray patterns showed no similarity

TABLE I Powder diffraction data for $Nb_6(InSb)$ in the β-W phase

2θ	d	I/I_0	hkl
30.1	2.969	47	111
34.1	2.629	80	200
38.2	2.356	100	210
42.1	2.146	73	211
62.4	1.488	47	222
63.9	1.457	20	320
66.5	1.406	40	321
71.75	1.315	20	400
77.1	1.237	38	411

Principle diffraction lines for an Nb–In–Sb alloy which was adopted on room temperature substrates and later annealed at 900° C for 3 h. Ni filtered CuKα ($\lambda = 1.5418$ Å) radiation was used in obtaining the diffraction pattern.