

# INTERFACE REACTION AND A SPECIAL FORM OF GRAIN BOUNDARY DIFFUSION IN THE Cr-W SYSTEM\*

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The two phase diffusion between chromium and tungsten, forming b.c.c. solid solutions, has been followed right from the beginning by means of a special X-ray diffraction technique, light microscopy and electron microprobe analysis. It appears that in a first stage only tungsten diffuses into the chromium, while the tungsten remains pure. The Kirkendall-effect however indicates that chromium is the much more rapidly diffusing component. It is shown that these two observations are not contradictory. In this stage the Cr-rich alloy can dissolve more tungsten than the equilibrium value; a thermodynamic explanation of this effect is given. A second stage consists of the formation of a W-rich alloy of a distinct composition in a discontinuous way at separate sites of the interface, presumably by an interface reaction. At the junction of the interface and a tungsten grain boundary a special form of grain boundary diffusion occurs, during which the grain boundary most likely moves away from its initial position, as in the case of discontinuous decomposition.

The experimental results are discussed in the form of an atomic description of the various phenomena, by taking into account the enormous difference in melting point of chromium and tungsten. This difference leads to a model of the atom and vacancy jumps at the interface right from the beginning of the diffusion; this model is based upon a much higher vacancy concentration in chromium compared to tungsten and a much greater mobility of the chromium atoms. From the considerations one might expect an "incubation time", during which the motion of Kirkendall-markers is delayed. An analogous atomic model has been used to give a description of the mechanism, by which the special form of the diffusion of chromium along a tungsten grain boundary occurs. In this boundary, treated as a phase with a very high vacancy concentration, it is proposed that a reaction should take place, leading to the deposition of a tungsten-rich W-Cr alloy, epitaxially to the adjacent chromium crystallite or to one of the adjacent tungsten crystallites. As a result the initial grain boundary will split into two boundaries or will move away from its original position.

## REACTION AUX INTERFACES ET DIFFUSION DE TYPE PARTICULIER AUX JOINTS DE GRAINS DANS LE SYSTEME Cr-W

La diffusion à deux phases entre le chrome et le tungstène formant des solutions solides c.c.c. a été étudiée depuis son démarrage par une méthode spéciale de diffraction des rayons X, par microscopie optique et par analyse à la microsonde électronique. Il apparaît que dans un premier stade, on assiste seulement à une diffusion du tungstène vers le chrome, alors que le tungstène reste pur. Cependant, l'effet Kirkendall montre que le chrome est le composant dont la diffusion est de beaucoup la plus rapide. L'auteur montre que ces deux observations ne sont pas contradictoires. Dans ce premier stade, l'alliage riche en Cr peut dissoudre plus de tungstène que la quantité correspondant à l'équilibre; l'auteur donne une interprétation thermodynamique de ce phénomène. Un second stade est constitué par la formation d'un alliage riche en tungstène de composition distincte, d'une manière discontinue et dans des régions de l'interface séparées les unes des autres, probablement par une réaction d'interface. Au jonction de l'interface, et sur un joint de grains de tungstène, il se produit un type spécial de diffusion aux joints de grains, au cours duquel le joint de grains se déplace le plus vraisemblablement loin de sa position initiale, comme dans le cas de la décomposition discontinue.

Les résultats expérimentaux sont discutés en envisageant une description atomique des différents phénomènes, tenant compte de l'écart très important entre les points de fusion du chrome et du tungstène. Cet écart conduit à imaginer, dès le début de la diffusion, un modèle de sauts des atomes et des dislocations à l'interface; il est basé sur une concentration en lacunes beaucoup plus élevée dans le chrome que dans le tungstène, et sur une mobilité beaucoup plus grande des atomes de chrome. A partir de ces considérations, on pourrait s'attendre à un "temps d'incubation" au cours duquel le mouvement des marqueurs de Kirkendall est retardé. Un modèle atomique analogue a été utilisé pour décrire le mécanisme par lequel se produit la diffusion spéciale du chrome le long d'un joint de grains de tungstène. Dans ce joint, traité comme une phase contenant une concentration en lacunes très élevée, on propose qu'il pourrait se produire une réaction conduisant au dépôt d'un alliage W-Cr riche en tungstène, en épitaxie sur le cristallite de chrome adjacent ou sur l'un des cristallites de tungstène adjacents. Il en résulterait, pour le joint de grains initial, un éclatement en deux joints ou un déplacement loin de sa position d'origine.

## GRENZFLÄCHENREAKTION UND EINE SPEZIELLE FORM DER KORNGRENZEN-DIFFUSION IM SYSTEM Cr-W

Die Zweiphasendiffusion zwischen den eine kubisch-raumzentrierte Legierung bildenden Metallen Chrom und Wolfram wurde vom Beginn der Diffusion an mit Hilfe einer speziellen Röntgenbeugungsmethode, optischer Untersuchungsverfahren und der Elektronen-Mikroanalyse untersucht. Es ergibt sich, daß im Anfangsstadium nur Wolfram in das Chrom diffundiert, während das Wolfram rein bleibt. Der Kirkendall-Effekt zeigt jedoch, daß Chrom die viel schneller diffundierende Komponente ist. Es wird gezeigt, daß sich diese beiden Beobachtungen nicht widersprechen. In diesem Stadium des Diffusionsprozesses kann die Cr-reiche Legierung mehr Wolfram lösen als der Gleichgewichtskonzentration entspricht; eine thermodynamische Erklärung dieses Effektes wird gegeben. Das zweite Stadium besteht in der Bildung einer W-reichen Legierung ganz bestimmter Zusammensetzung auf diskontinuierliche Weise

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und an verschiedenen Stellen der Grenzfläche; dies geschieht vermutlich durch eine Grenzflächenreaktion. Am Schnitt einer Grenzfläche mit einer Wolframkorngrenze findet eine spezielle Art der Korngrenzendiffusion statt, wobei sich die Korngrenze sehr wahrscheinlich wie bei der diskontinuierlichen Entmischung von ihrer ursprünglichen Lage fortbewegt.

Die experimentellen Ergebnisse werden anhand einer atomistischen Beschreibung verschiedener Phänomene diskutiert; dabei wird der enorme Unterschied in den Schmelzpunkten von Chrom und Wolfram berücksichtigt. Dieser Unterschied führt zu einem Modell, das Atom- und Leerstellensprünge in der Grenzfläche vom Beginn der Diffusion an voraussetzt. Dieses Modell geht davon aus, daß die Leerstellenkonzentration im Chrom viel größer ist als im Wolfram und daß die Chromatome eine viel größere Beweglichkeit besitzen. Aus diesen Betrachtungen würde man eine "Inkubationszeit" erwarten, während der die Bewegung der Kirkendall-Markierung verzögert wird. Ein analoges atomistisches Modell wurde zur Beschreibung des Mechanismus benützt, der zur speziellen Form der Diffusion von Chrom in einer Wolframkorngrenze führt. Es wird vorgeschlagen, daß in dieser als Phase mit sehr hoher Leerstellenkonzentration behandelten Korngrenze eine Reaktion stattfindet, die zur Ablagerung einer wolfram-reichen W-Cr-Legierung führt; diese Legierung ist epitaktisch zum angrenzenden Chrom-Kristallit oder zu einem der angrenzenden Wolfram-Kristallite. Als Folge wird die ursprüngliche Korngrenze in zwei Korngrenzen aufgespalten oder sie wird sich von ihrer ursprünglichen Lage fortbewegen.

### INTRODUCTION

From the extensive literature on binary intermetallic diffusion it appears that both the dependence of the chemical diffusion coefficient on composition and the magnitude of the Kirkendall-effect increases with the relative difference between the melting points of the pure metals. This appears to be the case at least in simple systems, in which the two components constitute a complete series of solid solutions or an incomplete series with a miscibility gap. In this respect the system chromium-tungsten may be predicted to be an extreme one: because of the very high melting point of tungsten with respect to that of chromium one can expect a pronounced decrease of the diffusivity with increasing tungsten content and a large Kirkendall-effect with a marker displacement in the direction of the Cr-rich part of the diffusion couple.

An additional point of interest of this system is that according to Greenaway<sup>(1)</sup> both metals are not completely soluble into each other below 1500°C. Figure 1 shows the simple miscibility gap, as determined by Greenaway, with the data given by Trzebiatowski *et al.*<sup>(2)</sup> When diffusion occurs at a temperature below the critical point, the couple will show a phase interface which will move when the diffusion flows in opposite directions across the interface are not equal. At such an interface a reaction is said to occur. Guy and Okawa<sup>(3)</sup> have made an attempt to show by calculation that the phase interface reaction is rate-determining in short diffusion times, but that diffusion in the adjacent phases becomes rate-controlling at progressively longer times. Because of the relatively slow reaction rate in the beginning the compositions at the interface may deviate from the equilibrium values, while in the later stage when this reaction is very rapid relative to the diffusion, interface equilibrium will be established. There is

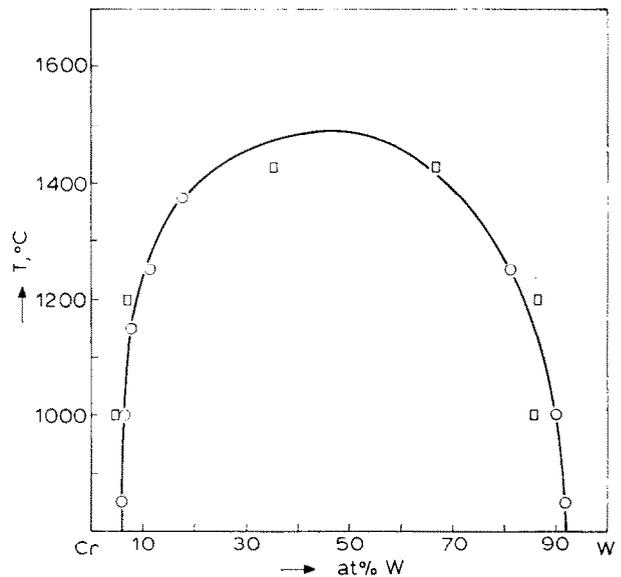


Fig. 1. Miscibility gap of the system Cr-W according to Greenaway (circles) and data from Trzebiatowski *et al.* (squares).

little experimental evidence of these equilibrium deviations. A review has been given by Eifert *et al.*<sup>(4)</sup> Dorward and Kirkaldy<sup>(5)</sup> found a supersaturation of copper in silicium, which could be ascribed to a retention in the formation of a new phase. Eifert *et al.*<sup>(4)</sup> however measured large deviations in Cu (f.c.c.)-Cu<sub>3</sub>Al (b.c.c.) diffusion couples at stages where the interface movement occurred practically diffusion-controlled. The authors reasoned that the necessary structural transformation for interface displacement was coupled with an inequality of the chemical potential of the more slowly diffusing component at both sides of the interface. It might however be argued that the more slowly diffusing component in that respect must be defined as that one which diffuses more slowly with respect to the *moving* interface

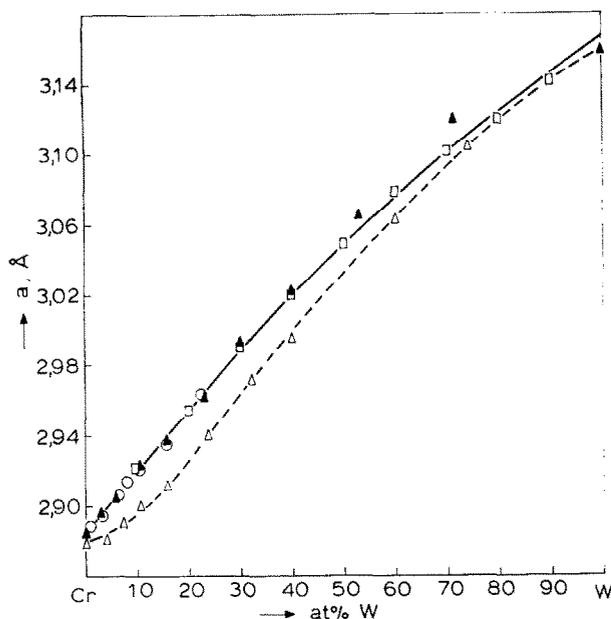


FIG. 2. Variation of the lattice constant with composition in the system Cr-W according to Greenaway (circles), Kubaschewski *et al.* (closed triangles), Trzebiatowski *et al.* (squares) and Pearson (open triangles).

instead of that one, defined by Eifert *et al.* as which diffuses more slowly with respect to the lattice. In a later paper Powell and Schumann<sup>(6)</sup> explained these deviations with non-equilibrium vacancy concentrations at both sides of the interface.

Little work has been done to investigate the mechanism of interface reactions. In an attempt to get information on the reaction in the system chromium-tungsten and to get a qualitative insight into the way the alloy phases form right from the beginning, we decided to follow the interdiffusion in this system by means of X-ray diffraction of layers close to the interface. This is possible by the appreciable variation of the lattice constant with composition, shown in Fig. 2,\* as determined by several workers.<sup>(1,2,7)</sup> To obtain supplementary information microprobe analysis was also carried out.

#### EXPERIMENTAL PROCEDURE

The X-ray technique which we used in our experiments was as follows: relatively thick (0.3 mm diameter) tungsten wires, both single- and polycrystalline, were electroplated with chromium. The

interdiffusion upon heating could be followed: (a) by choosing the initial outer chromium layer so thin ( $\sim 10 \mu\text{m}$ ) that in principle the whole diffusion zone became visible on one X-ray diffraction pattern; (b) by thinning the diffusion zone electrolytically down to about the desired radius and making an X-ray exposure. With the first technique we could follow the diffusion in one and the same wire couple after different heating times; with the second technique we obtained more precise information on the diffusion penetration in one couple after a certain diffusion time, but had to use more couples to study the time dependence.

Diffraction patterns were made with Cr-K $\alpha$  radiation in a 57.3 mm diameter cylindrical Debe-Scherrer camera, applying the Straumanis film loading method to be able to correct for film shrinkage, X-ray absorption and incorrect specimen centering. The wires were rotated perpendicularly to the incident beam. In this paper only the 211-back reflections are shown, since these are the most sensitive to lattice constant variation and thus most illustrative.

The tungsten wires were (a) so-called "chloride process" bars<sup>(10)</sup> of about 2 mm thickness, which were thinned electrolytically to about 0.35 mm diameter wire, (b) single crystalline "Pintsch"-wire<sup>(11)</sup> and (c) 0.30 mm diameter polycrystalline wire. The Pintsch-wire contained 2 wt. % ThO<sub>2</sub> in the form of very small ( $\sim 1 \mu\text{m}$  size) particles, which could be used as Kirkendall-markers.

After cleaning, electrolytic degreasing and polishing, the wires were electroplated with chromium, using a bath of 250 g/l CrO<sub>3</sub> and 2.5 g/l H<sub>2</sub>SO<sub>4</sub> at 80°C with a current density of 55 A/dm<sup>2</sup>.<sup>(12)</sup>

To obtain supplementary information besides the X-ray results and to study the interdiffusion quantitatively, sandwich-couples were prepared for microprobe analysis. For this purpose chromium crystals, supplied by Fluka A.G., Switzerland (purity 99.997%) were re-arc-melted into buttons, which were cut into planparallel discs, 2.0 mm thick and 7.0 mm diameters, by spark machining and subsequently grinding and polishing. The tungsten part was plate material, 0.3 mm thick, supplied by Drijfhout, Holland (purity 99.98%). Welding of the sandwich couples Cr-W-Cr was accomplished by passing an electric current (150 A) for 10 sec through the couple in an argon-arc furnace, of which the upper movable tungsten electrode was replaced by a copper contact. In a specially constructed specimen holder (Fig. 3) the couple parts were piled up in a sequence graphite-Cr-W-Cr-graphite. The graphite discs *K* (10 mm diameters, 5 mm high) serve to prevent too high

\* Here it is necessary to point out that Greenaway's measurements,<sup>(1)</sup> as summarized by Pearson,<sup>(8)</sup> do not agree with those of the other investigators.<sup>(2,7)</sup> This is due to incorrect use of Greenaway's paper:<sup>(9)</sup> contrary to the data in Fig. 4, those of Fig. 5 and 6 are in excellent agreement with the other determinations. It is also practically certain<sup>(8,9)</sup> that the tabulated lattice constants in the cited literature are given in KX-units. Figure 2 has been obtained after correction for the difference between KX- and Å-units.

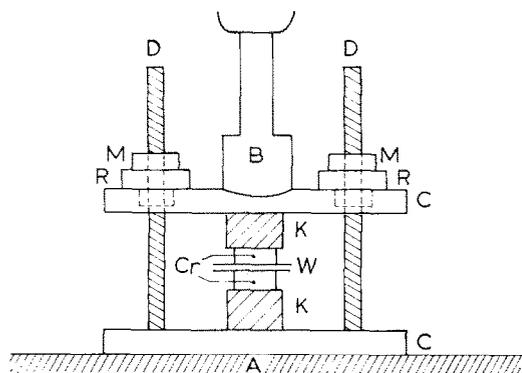


Fig. 3. Specimen holder for resistance welding the diffusion couples Cr-W-Cr.

currents. The holder consists of two parallel copper plates *C* ( $55 \times 20 \times 4$  mm) which are electrically isolated from each other. The distance between these plates could be varied by moving the upper plate along two stainless steelen bolts *D*, fixed to the lower plate. Between both plates the couple parts were clasped with slight pressure by turning on two nuts *M*, which are separated from the upper plate by two insulating rings *R*. The holder with sample was placed on the copper ground plate *A* of the argon-arc furnace, after which during evacuation of the furnace electrode *B* was put in a shallow concavity of the upper copper plate. The pressure on the couple parts could be varied by reducing the atmospheric pressure on the bellow (attached to the movable electrode) by means of a counterweight, or by varying the argon pressure inside the furnace. In our experiments a pressure of  $15 \text{ kgf/cm}^2$  on the couple parts appeared sufficient for successful welding. In those cases where the couple parts were nearly planparallel the contact between the metals was excellent. Interdiffusion during this resistance welding did not occur to a measurable extent.

To study the Kirkendall-effect the tungsten plate was covered with a thin  $\text{ThO}_2$ -layer by means of electrophoresis from a suspension of  $\text{ThO}_2$  in absolute ethylalcohol, containing a trace  $\text{Th}(\text{NO}_3)_2$ , at 300 V. After welding this  $\text{ThO}_2$ -powder appeared to be conglomerated to  $\sim 3 \mu\text{m}$  size particles which did not measurably act as diffusion barriers.

The couples were heated in closed silica tubes. After evacuation these were filled with purified argon to an internal pressure which became about 1 atm at the heating temperature. The tubes were hung from a platinum wire in a vertical silboride-tube furnace, through which a gas stream of purified argon was maintained. The diffusion treatment was finished by dropquenching the tubes into icewater. Neither

oxidation of the sample, nor reaction with silica took place.

## RESULTS

### 1. X-ray diffraction analysis

The diffusion experiments were carried out in the temperature range between 1250 and 1600°C. The latter temperature is about 100°C higher than the critical temperature of the miscibility gap according to Greenaway (Fig. 1).

Figure 4 illustrates a series of diffraction patterns from one and the same single crystalline "chloride" tungsten wire, plated with  $\sim 10 \mu\text{m}$  chromium, after heating successive times at 1250°C. Pattern *a* was obtained after a low temperature treatment (800°C) to relieve the stress and to recrystallize the chromium, and shows, before the interdiffusion, diffraction spots from the tungsten single crystal and a diffraction ring from pure polycrystalline chromium. After 11 hr diffusion pattern *b* demonstrates that a secondary recrystallization of the chromium has occurred to form a crystal that is in parallel orientation to the tungsten crystal.\* The chromium reflections exhibit

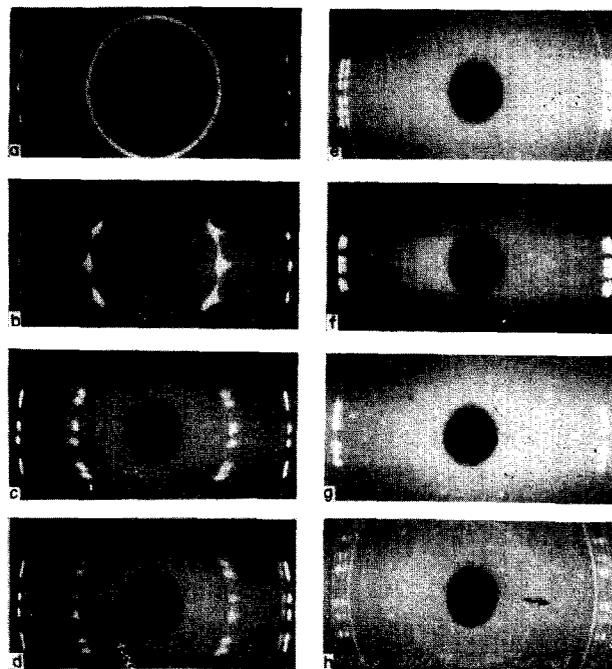


Fig. 4. Cr-K $\alpha$  diffraction patterns, showing the 211-back reflections from a chromium-plated tungsten single crystal after diffusion at 1250°C for: (a) 0 hr; (b) 11 hr; (c) 20 hr; (d) 25 hr; (e) 38 hr; (f) 50 hr; (g) 60 hr; (h) is a pattern from a Cr-plated Pintsch-wire after 55 hr diffusion (see footnote † on page 323).

\* Such a "parallel" recrystallization did not always take place with different tungsten-wires. From our experiments it appeared that the particular crystallographic orientation of the tungsten wire determines whether it occurs.

streaks in the direction of a higher lattice constant (these reflections are, as in the other patterns, back reflections). This means that tungsten has diffused into the chromium, forming a series of alloys from pure chromium at the surface to a Cr-rich alloy (presumably saturated with tungsten) at the Cr-W interface.

Contrary to the chromium reflections the tungsten spots have *not* moved and do not show streaks in a direction corresponding to a decreasing lattice constant. This means that chromium has practically *not* diffused into the tungsten, although at this temperature tungsten may contain about 19 at. % Cr in solid solution (see Fig. 1).

After 20 hr diffusion at 1250°C (*c*) the reflections of the Cr-rich phase have moved further to a position corresponding to an increased lattice constant. From the broadness of the reflections we calculated the composition of the Cr-rich phase, ranging from 10.5 to 14.5 at. % W. The latter value is striking, since the solubility limit at 1250°C is 11.5 at. % W. As in the former pattern the tungsten reflections have still not moved, indicating that the tungsten has remained pure. However, some very faint reflections (see arrow) have appeared, parallel to those from the tungsten. These correspond to a W-rich phase with a distinct composition of 86 at. % W. A remarkable detail of the appearance of this phase in the diffraction pattern is that its reflections are not of the same intensity above and below the equator. Evidently this phase has nucleated and grown a small amount locally on one side of the tungsten wire producing a 211-reflection above the equator, but has probably not yet or hardly formed on the opposite side of the wire, which accounts for the absence of the corresponding  $\bar{2}\bar{1}\bar{1}$ -reflection below the equator.

This W-rich phase has grown after 25 hr (*d*\*) and it is noticeable (as in pattern *c*) that its reflections (corresponding to 84 at. % W) are clearly separated from those of pure tungsten, indicating the absence of intermediate compositions between 84 and 100 at. % W. This fact and our observation that the time necessary to develop this phase increased very much with the thickness of the initial chromium layer, suggest that the W-rich phase has developed "discontinuously" by an *interface reaction* between the saturated Cr-rich phase and pure tungsten. The reaction goes probably by the supersaturation of the Cr-rich phase, noted in pattern *c*. This idea is supported by pattern *h*, which has been obtained in the

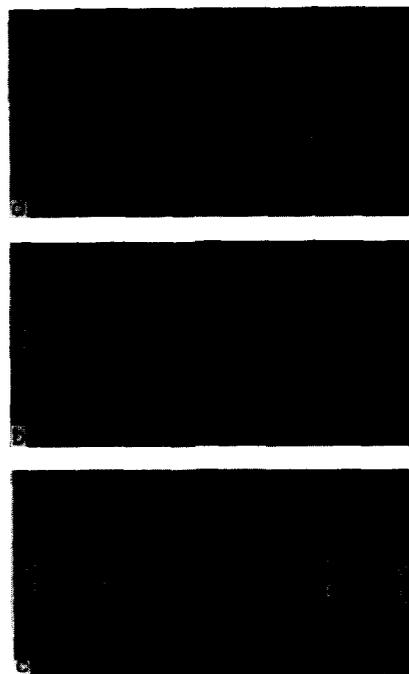


FIG. 5. 211-reflections from a chromium-plated polycrystalline tungsten-wire after diffusion at 1250°C for: (a) 3 hr; (b) 16 hr; (c) 24 hr.

course of a similar diffusion experiment with a Cr-plated Pintsch-wire. In this pattern,† besides the reflections from the W-rich phase and pure tungsten, the spots (see arrow) of a Cr-rich phase corresponding to a tungsten content of 16.5 at. % W, i.e. a supersaturation of 5 at. %, are visible. The supersaturation was also observed at higher diffusion temperatures, generally in a stage in which the W-rich phase had not yet formed. After 38 hr (*e*) the reaction has been completed at the total expense of the Cr-rich phase, after which the ultimate alloy then forms by "normal" diffusion (*f*, *g*).

Using polycrystalline tungsten wire, the results were practically the same. Pattern *a* in Fig. 5 demonstrates that after 3 hr diffusion at 1250°C only tungsten has diffused into the polycrystalline chromium and not the reverse, while after 16 hr diffusion (*b*) the W-rich phase (see arrow) has again formed "discontinuously" with a composition of 87 at. % W. After prolonged diffusion (pattern *c*) the W-rich phase has grown, while its composition has changed to 84 at. % W. Assuming that the latter value corresponds to the solubility limit, it thus appears that the W-rich phase is initially undersaturated to chromium.

\* The arrow in this pattern points to an irrelevant Cr-K $\beta$  220<sub>W</sub> reflection.

† This pattern shows a number of additional diffraction rings, due to the presence of a Cr-W carbide (Cr, W)<sub>23</sub>C<sub>6</sub>; this compound has formed by carbon diffusion from the Pintsch-wire into the chromium.

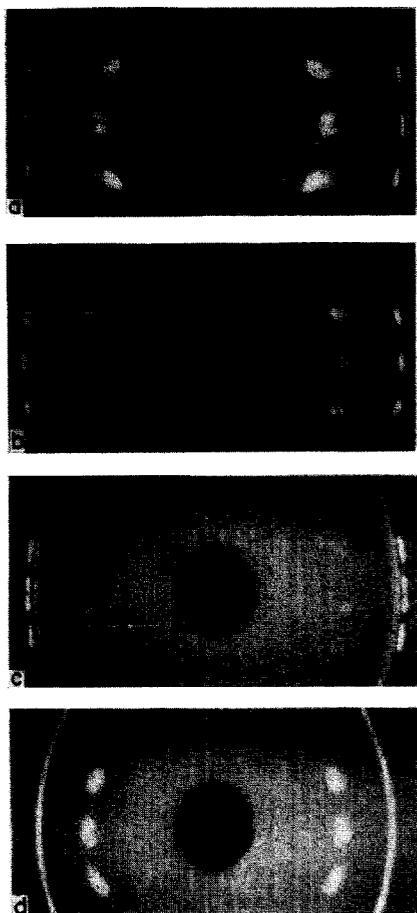


FIG. 6. 211-reflections from an etched chromium-plated single crystalline tungsten wire after diffusion at 1600°C for: (a) 1 hr; (b) 1 hr, longer etch; (c) 4 hr; (d) 18 hr.

The course of the interdiffusion and reaction process appeared to be practically the same at higher temperatures, i.e. 1400 and 1500°C. It was however noticed that also at 1600°C, i.e. 100°C higher than the critical temperature of the miscibility gap, no complete series of solid solutions were formed: Fig. 6 shows a series of diffraction patterns, which were obtained after diffusing a single crystalline tungsten wire, plated with a relatively thick (50  $\mu\text{m}$ ) chromium layer. The exposures were made after etching off so much of the chromium layer that the reflections from the W-rich side of the interface also appeared clearly on the patterns. After 1 hr diffusion pattern *a* shows again that tungsten has diffused into the chromium, while the tungsten has remained pure. By etching a longer time and making an X-ray exposure, pattern *b* reveals that there are no alloys formed with compositions between 32.5 at. % W and pure W (see footnote \* on p. 323).

After 4 hr diffusion (pattern *c*) however a *poly-*

*crystalline* W-rich phase (composition ranging from 70 to 90 at. % W) has formed, lying between the two parallel oriented crystals of pure tungsten and the Cr-rich phase. Phases with central compositions are still not present. After 18 hr diffusion (pattern *d*) it appears that the new polycrystalline W-rich phase has grown to such extent that the reflections of pure tungsten are not visible any more. It was observed that after prolonged etching the reflections of single crystalline tungsten appeared again (pattern not shown). The formation of the polycrystalline intermediate layer of a W-rich alloy is very probably the result of a recrystallization of the tungsten, accompanied by a very rapid grain boundary diffusion of chromium.

The absence of solid solutions with central compositions is not in agreement with the phase diagram of Fig. 1. In order to investigate whether the critical temperature of the miscibility gap is actually higher than 1500°C, a 50 at. % Cr-W alloy, prepared by sintering the mixed metal powders under a hydrogen atmosphere at 2000°C, had been annealed at 1600°C. In agreement with the diffusion results this alloy decomposed at the latter temperature into a Cr-rich and W-rich solid solution (Fig. 7). Metallography showed that the decomposition mode was of the cellular type, as already observed at lower temperature by Porter.<sup>(13)</sup> From our results we conclude that the critical point of 1500°C is not correct; we estimate it at about 1650°C.

A particular phenomenon was encountered when using Pintsch-wire in the diffusion experiments. After diffusion has taken place to some extent, diffraction lines from  $\text{ThO}_2$  appear clearly on the

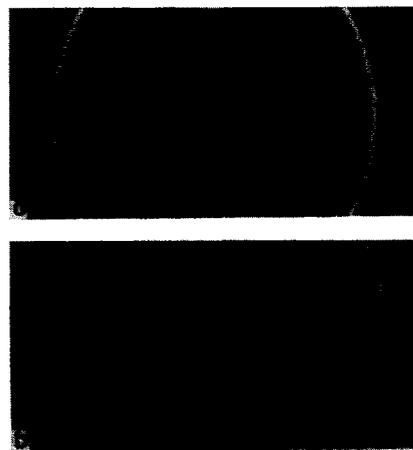


FIG. 7. 211-reflections from a 50 at. % Cr-W alloy, sintered at 2000°C; (a): as-quenched; (b) after aging for 4 hr at 1600°C; the additional inner and outer ring come from respectively a Cr-rich and a W-rich phase.

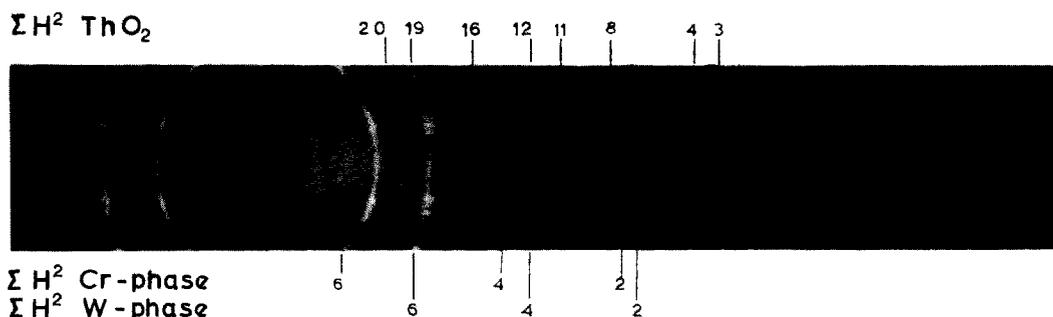


FIG. 8. Complete X-ray diffraction pattern from a chromium-plated Pintsch-wire, after diffusion at 1400°C for 96 hr, showing additional ThO<sub>2</sub>-diffraction lines.

X-ray patterns, see Fig. 8. These reflections are *not* visible on a pattern from an undiffused Pintsch-wire under the same exposure conditions. We suggest that the ThO<sub>2</sub>-particle density near the phase interface increases due to Kirkendall-motion of the particles in the direction of a higher chromium content (see below).

#### MICROSCOPY AND MICROPROBE ANALYSIS

##### 1. Kirkendall-effect

From the diffraction patterns one is tempted to conclude that tungsten diffuses intrinsically more rapidly than chromium. It must however be emphasized that the diffraction results only indicate that *in* the Cr-rich phase the chemical diffusivity is much larger than *in* practically pure tungsten, irrespective of the atomic mechanism. The diffusion of chromium into tungsten is so slow that it could not be detected by our means. In order to determine which is atomically the more rapidly diffusing component, one has to ascertain the direction of the Kirkendall-effect. As an example Fig. 9(a), which is a Th-L $\alpha$  image of a chromium-plated Pintsch-wire (after 50 hr diffusion at 1250°C), shows that some ThO<sub>2</sub>-particles, originally present in the Pintsch-wire, have moved a certain distance into the chromium. A similar image is Fig. 9(b) (after 96 hr diffusion at

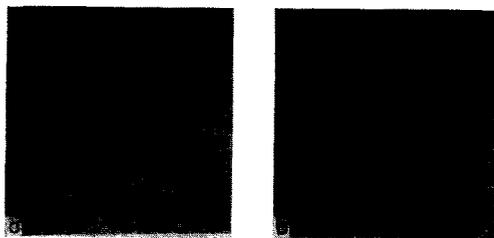


FIG. 9. Electron-microprobe Th-L $\alpha$  emission images from a chromium-plated Pintsch-wire, showing the outward displacement of ThO<sub>2</sub>-particles: (a) after 50 hr diffusion at 1250°C, 500 $\times$ ; (b) after 96 hr diffusion at 1400°C, 250 $\times$ .

1400°C; cf. Fig. 8) which shows an enrichment of ThO<sub>2</sub>-particles at the outer surface of the chromium and a densification of these particles at the phase interface. The latter observation agrees with the appearance of ThO<sub>2</sub>-diffraction lines, as mentioned before.

The Kirkendall-effect manifested itself also in the usual way in sandwich diffusion couples with ThO<sub>2</sub>-markers initially at the joint. Figures 10(a) and (b) (an electron reflection image and a Th-L $\alpha$  image) show the ThO<sub>2</sub>-marker-displacement from the interface after 16 hr diffusion at 1600°C. (From the penetration curve it was calculated that the Matano-interface in this example practically coincides with the phase interface.)

A particular appearance of the Kirkendall-effect has been observed with a thin bimetal couple. On a 20  $\mu$ m thick tungsten foil a chromium

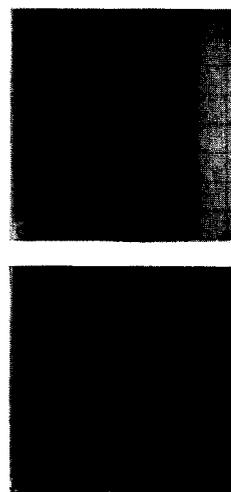


FIG. 10. Electron-microprobe images from a Cr-W diffusion couple near the interface (Cr left, W right) after 16 hr diffusion at 1600°C, showing the Kirkendall-displacement of ThO<sub>2</sub>-marker particles from the interface in the direction of the Cr, 250 $\times$ : (a) electron-image, the brightness discontinuity corresponds to the interface; (b) Th-L $\alpha$  emission image.

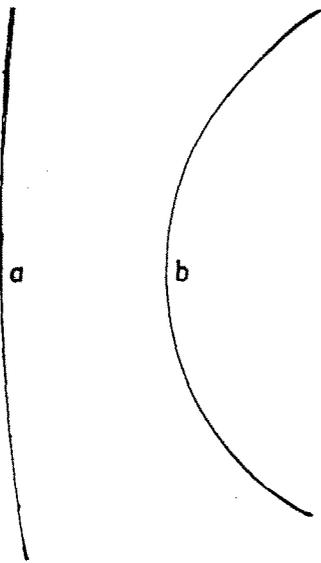


FIG. 11. (a) Chromium-tungsten foil before diffusion, hollow side chromium; (b) the same after 50 hr diffusion at 1250°C, hollow side chromium, 12 $\times$ .

layer of about 6  $\mu\text{m}$  had been vacuum-evaporated at 1000°C. When this foil is cooled to room temperature it bends due to the greater thermal shrinkage of chromium. [Figure 11(a), chromium at the inside.] When heated up to 1000°C the foil stretches again, while above this temperature the bending reverses.

However, after heating a long time (16 hr) at 1250°C and cooling to room temperature, the radius of the bend has considerably increased in the original direction [Fig. 11(b)]. Apparently the Cr-rich part shrinks laterally during diffusion, while the W-rich part expands laterally. This is in agreement with the direction of the Kirkendall-effect, according to which vacancies flow from tungsten to chromium. In semi-infinite diffusion couples edge dislocations with a Burgers-vector parallel to the diffusion direction climb laterally in order to maintain vacancy equilibrium and cause a longitudinal shrink and expansion of the lattice in both parts of the couple.<sup>(14)</sup> In our particular example of the foil-couple however, apparently also edge dislocations with a Burgers-vector perpendicular to the diffusion direction climb and cause lateral dimension changes. Under the assumption that the foil couple is composed of two single crystals, it follows from the bend radius after diffusion that  $\sim 10^8$  dislocations/cm<sup>2</sup> have moved out of the couple, a number which is not unreasonable as an order of magnitude.

A similar foil-bending has been observed by Liu and Powell.<sup>(15)</sup> The magnitude of the Kirkendall-effect in the Cr-W system is such that the intrinsic

diffusion coefficient of chromium is about 80 times that of tungsten. This ratio was found at a composition of 2 at. % W, using pure metal couples.<sup>(16)</sup> Thus, we may conclude that, while tungsten dissolves much more rapidly into chromium than vice versa, chromium is atomically the more rapidly diffusing component.

## 2. The appearance of the tungsten-rich phase

(a) *Single crystalline tungsten.* In agreement with the X-ray diffraction results it appears microscopically that the W-rich phase does not develop initially as a continuous film, but forms at separate sites at the interface [Figs. 12(a)-(c)]. It is striking that the W-rich phase is rather homogeneous in composition. Besides the regions of the new W-rich phase have the appearance of etch pits viewed from the side. Diffusion of chromium into tungsten at sites away from these "pits" could not be detected with the electron microprobe. One might attribute these "etchpits" to an enhanced diffusion of chromium along dislocations which emerge from the tungsten or to an enhanced nucleation of the W-rich phase at these intersections. On the other hand, according to Rieck,<sup>(17)</sup> "doped" single crystalline tungsten wires have a fragmented structure and it is likely that a rapid diffusion takes place along the low-angle grain boundaries between the fragments. Especially the boundaries which lie more or less perpendicular to the wire axis might be effective short-circuit paths, because the dislocations which constitute these

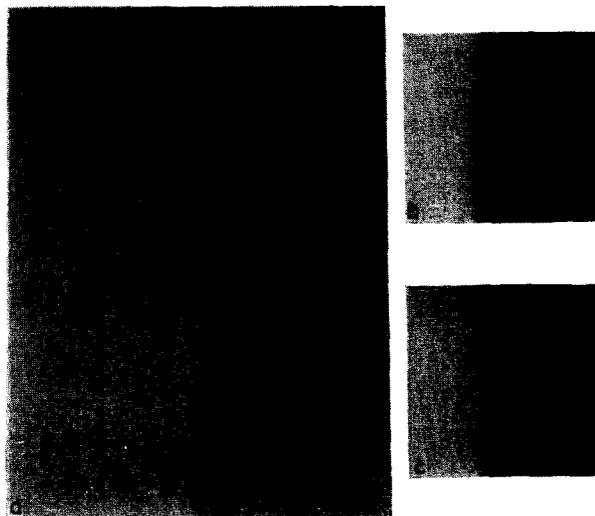


FIG. 12. (a) "Etch pits" of W-rich phase at the interface of a chromium-plated Pintsch-wire after 21 hr diffusion at 1400°C, 480 $\times$ ; (b), (c) corresponding electron microprobe Cr-K $\alpha$  emission images, 500 $\times$ .

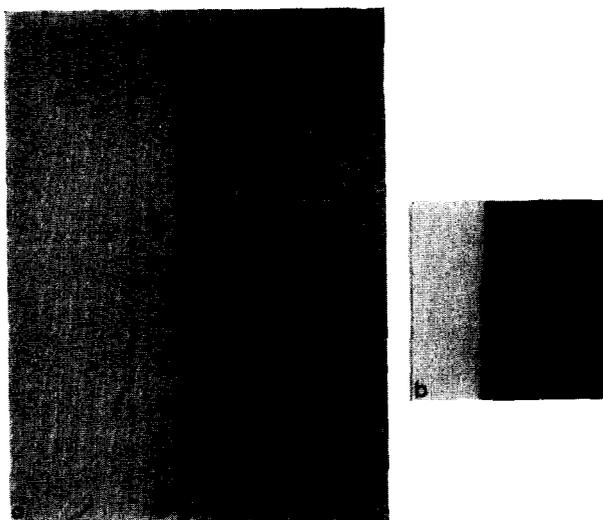


Fig. 13. (a) Formation of the W-rich phase (arrow) at the junction of a tungsten grain boundary and the interface after 6 hr diffusion at 1400°C, 480 $\times$ ; (b) corresponding electron microprobe Cr-K $\alpha$  emission image, 500 $\times$ .

boundaries have cores which lie parallel to the diffusion direction.

(b) *Polycrystalline tungsten.* In polycrystalline tungsten the W-rich phase forms initially mainly at the junctions between tungsten grain boundaries and the interface [Figs. 13(a) and (b)]. The appearance of the new phase (see arrow) is similar to the above mentioned "etchpits", in the sense that its composition does not change in a direction parallel to the interface (see image b). This is unusual for grain boundary diffusion: normally the slow volume diffusion from the grain boundary into the adjacent crystals compared to the rapid diffusion along the boundary results in a steep concentration decrease away from the boundary (the well-known Fisher model<sup>(18)</sup>). In our case the constancy in composition

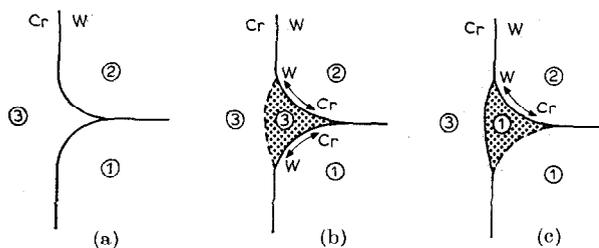


Fig. 14. Schematic illustration of proposed formation of the W-rich phase at the junction of a tungsten grain boundary and the interface: (a) initial grain boundary groove; (b) nucleation and growth of the W-rich phase, epitaxially to the chromium-grain 3, grain boundary "splitting"; (c) nucleation and growth of the W-rich phase epitaxially to the tungsten-grain 1; grain boundary motion in the direction of grain 2. The full lines are incoherent, the broken lines coherent interfaces.

in a broad range around the grain boundary and the microstructures do suggest that the grain boundary actually moves during diffusion. The following reasoning also leads to this proposition: referring to the supersaturation of the Cr-rich phase in contact with pure tungsten, as revealed by the X-ray diffraction results, one may suppose that from a thin supersaturated layer a W-rich phase nucleates most easily at the junction of a tungsten grain boundary and the phase interface. Figure 14(a) represents schematically such a junction, at which a W-rich phase nucleates, in Fig. 14(b) epitaxially to the adjacent chromium crystallite (orientation "3"), in Fig. 14(c) epitaxially to one of the tungsten crystallites (in the sketch orientation "1"). In the first case the grain boundary 1-2 "opens" as during the penetration of a liquid into a grain boundary and "splits" into two new grain boundaries 1-3 and 2-3; in the second case the grain boundary 1-2 moves away from its initial position. In both cases the W-rich phase can grow by grain boundary diffusion and motion. During its motion the grain boundary remains a short-circuit for rapid diffusion, leading to a more effective homogenization than when it is fixed, as is usually the case.

This mechanism of nucleation and diffusional growth of a new phase along a grain boundary is to some extent analogous to the mechanism of discontinuous (cellular) decomposition, where the boundary moves in the direction of a supersaturated crystal and leaves behind a transformed cellular crystal.

Figure 15(a) shows an example of this decomposition mode at one and the same grain boundary in a 20 at. % W Cr-W alloy, which had been aged at 1250°C. The duplex cells, consisting of lamellae of a Cr-rich and a W-rich phase, have grown into the matrix crystals [see schematic interpretation in Fig. 15(b)], at separate sites in opposite directions; the original smoothly curved boundary has changed into one with a very complex form (according to Smith<sup>(19)</sup>).

The similarity between decomposition and diffusion at a grain boundary is very pronounced after sectioning the diffusion couple perpendicularly to the diffusion direction. Figures 16(a) and (b) and Fig. 17 show the typical microstructure of pure tungsten crystallites, between which the "broadened" grain boundaries contain a homogeneous W-rich phase (16 at. % Cr). Figure 18(b) is a Cr-K $\alpha$  emission image from the same area as shown by Fig. 18(a). It demonstrates the homogeneity of the W-rich phase, next to the purity of the tungsten crystallites. The "alternating character" of the W-rich phase indeed

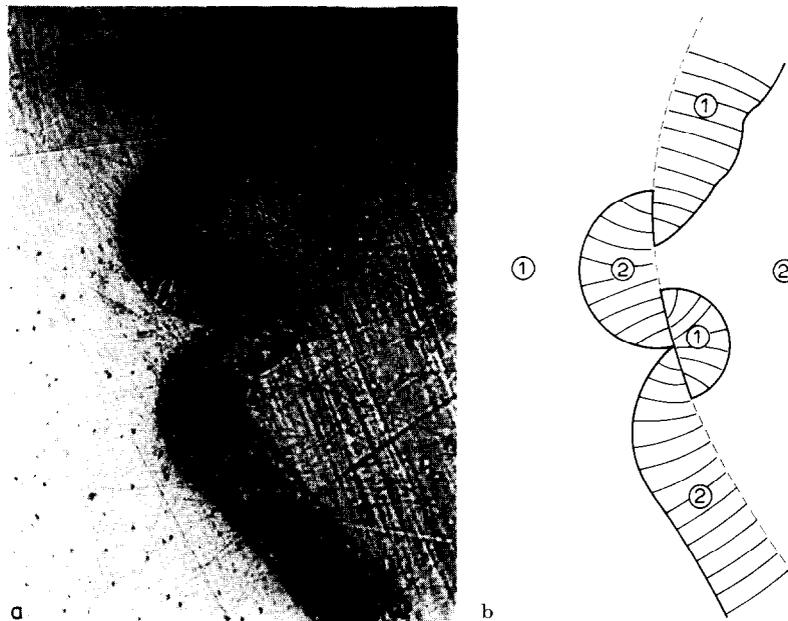


FIG. 15. (a) Discontinuous decomposition of a Cr-W alloy at a grain boundary, 570 $\times$ ; (b) schematic interpretation of micrograph (a); the broken line is the original position of the grain boundary, the full line represents the grain boundary after decomposition.

suggests that during the diffusion the grain boundaries actually have moved, into one direction or the other, leaving behind in their trace the W-rich phase.

To clarify our interpretation of the microstructures, we sketched in Fig. 19(a) a grain boundary between tungsten crystallites "1" and "2" and the W-rich phase with its specific orientation "1" or "2", depending on the grain from which it has grown away [cf. Fig. 14(c)]; between *A* and *B* a partial "overlapping" has occurred, as is usually also observed in the case of discontinuous decomposition. Figure 19(b) is a schematic interpretation of the lower

boundary in Fig. 17, in which we assume that between *A* and *B* grain boundary "splitting" [cf. Fig. 14(b)] has occurred and between *B* and *C* motion in an upward direction. It has to be noted that the proposed orientation relationships have not yet been verified experimentally. This could be achieved by means of selected area X-ray or electron diffraction techniques.

#### DISCUSSION

##### 1. Initial atomic displacements at the interface and the Kirkendall-effect

In the first stage of the mixing process a rapid diffusion in the Cr-rich part takes place whereas the



FIG. 16. (a), (b) Microstructures of polycrystalline tungsten, showing the diffusion of chromium along tungsten-grain boundaries (16 hr, 1400°C), 350 $\times$ ; cross section perpendicular to the diffusion direction.

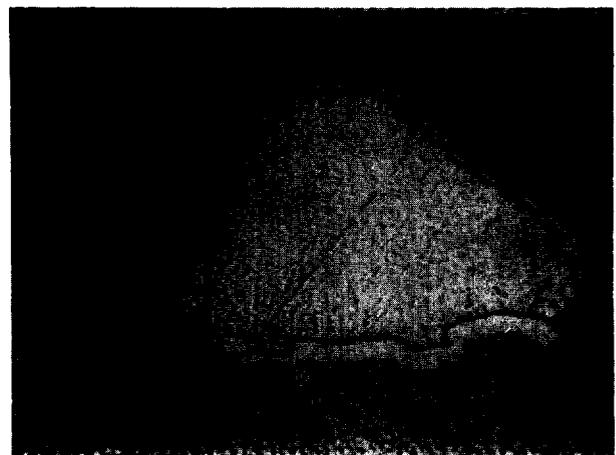


FIG. 17. Idem Fig. 16; 900 $\times$ .



FIG. 18. (a) Idem Fig. 16; 500 $\times$ ; (b) corresponding electron microprobe Cr-K $\alpha$  emission image, 240 $\times$ .

tungsten remains pure. Although this is an observation on a still macroscopic scale because of the limitation of our detection possibilities, this result is however so striking that it has led us to consider which atom jumps might occur in the very first stage at the interface between pure chromium and pure tungsten (Fig. 20).

From self diffusion data<sup>(20,21)</sup> and calculations of activation energies of vacancy formation and vacancy migration in the pure metals<sup>(22)</sup> one may estimate that at a temperature of 1250°C for instance the vacancy concentration of pure chromium is about  $10^6$  times the vacancy concentration of pure tungsten.

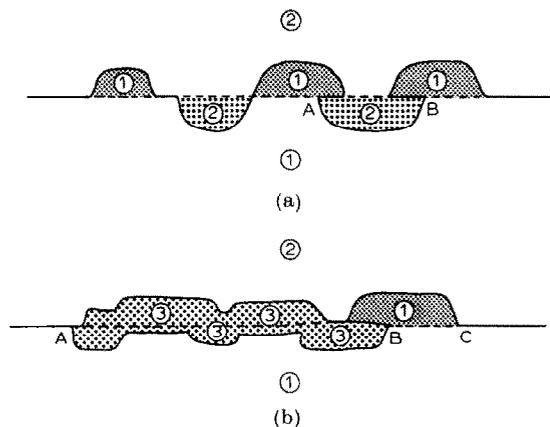


FIG. 19. (a) Schematic interpretation of form and orientation of the W-rich phase at a tungsten-grain boundary in a plane which is perpendicular to the diffusion direction; the broken line is the original position of the grain boundary, the full line is the displaced grain boundary [cf. Fig. 14(c)]; (b) schematic interpretation of lower grain boundary in Fig. 17. Between A and B the W-rich phase has the orientation "3" of the adjacent chromium-grain [cf. Fig. 14(b)], between B and C the orientation of the W-grain 1.

whereas the ratio between the respective vacancy mobilities in these metals is about  $10^3$ . From these values it is probably justified in order to simplify our considerations, to ignore the presence of vacancies in the tungsten and to assume that a given vacancy interchanges preferentially with a Cr-atom in a surrounding of both kinds of atoms; the latter assumption moreover is in agreement with the direction of the Kirkendall-effect.

The initial situation is schematically represented by Fig. 20(a) with no vacancies in tungsten and 4 vacancies in chromium, where these are constantly in motion. According to this extreme situation Cr-atoms cannot diffuse directly into the tungsten lattice. On the contrary, once in the many times a vacancy in

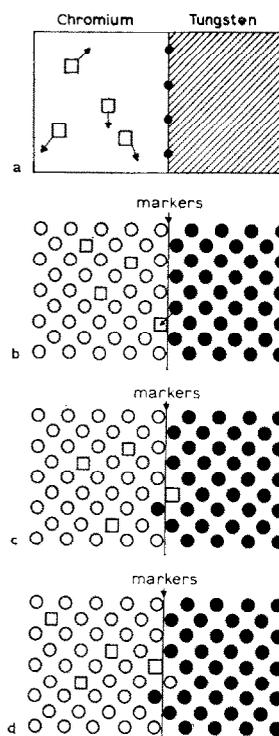


FIG. 20. Proposed atom jumps at the interface between chromium and tungsten at the beginning of the diffusion. Open circles: Cr-atoms, black circles: W-atoms, squares: vacancies, see text.

the chromium reaches the boundary, a W-interface atom may jump into this vacancy (b), bringing the latter to the tungsten side of the boundary (c). This situation is energetically unfavourable because the tungsten has now a vacancy in surplus and the chromium "lacks" one vacancy. Since the Cr-atoms jump so often compared to the W-atoms, this situation will be restored immediately by a subsequent Cr-atom jump into this vacancy, bringing the latter back in the chromium (d). Actually any such W-atom jump

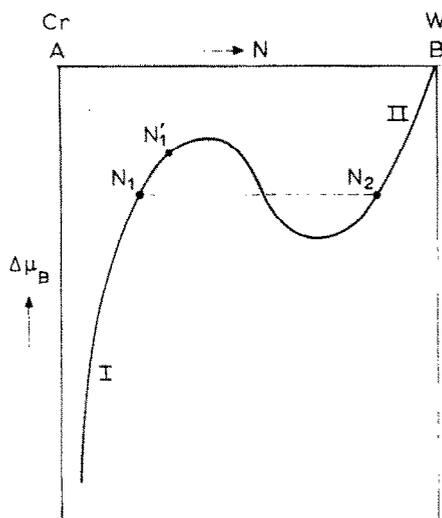


FIG. 21. Schematic variation of the relative chemical potential of component  $B$  ( $W$ ) in a binary system  $A-B$  ( $Cr-W$ ) with a miscibility gap at a temperature below the critical point.  $N_1$  and  $N_2$  are equilibrium compositions,  $N_1'$  represents a supersaturated  $Cr$ -rich alloy.

is followed by a correlated  $Cr$ -atom jump, virtually a mechanism of *direct interchange by means of a vacancy*. During these direct interchanges there is no net vacancy flow. This would mean that fiducial, infinitely small markers, initially located at the interface, would not shift in the beginning with respect to the outer ends. This is contrary to Darkens expression of the Kirkendall-velocity,<sup>(23)</sup> being infinitely large at  $t = 0$ .

The  $W$ -atoms which have jumped across the interface can diffuse away in pure chromium by means of the effective vacancies in this metal. However every  $Cr$ -atom which replaces a  $W$ -interface atom cannot penetrate the tungsten lattice because of the absence of vacancies. Consequently the chromium concentration at the interface remains high and the tungsten remains essentially pure. The phase interface between pure tungsten and the  $Cr$ -rich alloy gradually moves away from the marker interface in the direction of pure tungsten. When these markers, in reality not infinitely small, but large compared to the atoms, get completely loose from the interface, a  $Cr$ -rich alloy is formed between these markers and the interface with vacancies in thermal equilibrium, the concentration of which does not differ very much from that on the other side of the markers. From about that time it is suggested that marker motion sets in: the unequal diffusion flows of  $Cr$ - and  $W$ -atoms in both directions past the markers would then give rise to a net vacancy flow. Consequently at the  $Cr$ -rich side of the markers a surplus of vacancies, at the  $W$ -rich side of the markers

in the region between the markers and the phase interface a deficit of vacancies with respect to thermal equilibrium will occur. The necessary maintenance of this equilibrium will then be brought about by "positive" dislocation climb at the  $Cr$ -rich side of the markers and by "negative" climb at the other side in the thin  $Cr$ -rich layer between the markers and the phase interface.

Thus marker motion starts after a certain time interval which is primarily necessary to loosen the markers from the phase interface. This delay time will be determined by the marker size and the rate of dissolution of the tungsten into the chromium.

The effect is therefore estimated to be small in our experiments where the markers had a size of  $1-4 \mu m$ . Actually we were not able to detect such a delay time, presumably because of the scatter of marker position data. Besides it was noted that recrystallization phenomena took place in the  $W$ -rich region after longer diffusion times, which caused a nonparabolic motion of the phase interface from the marker interface.

## 2. Supersaturation of the $Cr$ -rich alloy

Bearing in mind that the gradient of the chemical potential of a component is the driving force for its diffusion, Fig. 21 represents schematically the variation of this quantity of component  $B$  (tungsten) in a binary system  $A-B$  ( $Cr-W$ ) at a temperature below the critical point of the miscibility gap.<sup>(24)</sup> When  $A$  and  $B$  dissolve into each other with the same rate, then  $\mu_B$  rises along I in the  $A$ -rich part and falls along II in the  $B$ -rich part of the couple (the reverse holds for  $\mu_A$ ) until equilibrium between the two phases is established when  $\mu_{B1} = \mu_{B2}$  (and  $\mu_{A1} = \mu_{A2}$ ) at compositions  $N_1$  and  $N_2$ . When in the  $Cr-W$  system initially only tungsten dissolves in the chromium,  $\mu_W$  rises in the  $Cr$ -alloy, but its value remains lower than the standard value  $\mu_W^0$  of pure tungsten. Thus more tungsten may diffuse into the  $Cr$ -rich phase, making an interface layer supersaturated with respect to tungsten (composition  $N_1'$ ). This supersaturation will occur when nucleation difficulties arise in the formation of the  $W$ -rich phase with composition  $N_2$ . However near special sites at the interface where the  $W$ -rich phase forms easily (dislocations and grain boundaries) the adjacent  $Cr$ -rich phase will have composition  $N_1$ .

## 3. Formation and growth of the $W$ -rich phase at a tungsten grain boundary

In the following an attempt is made to give an atomic description of the formation and growth of

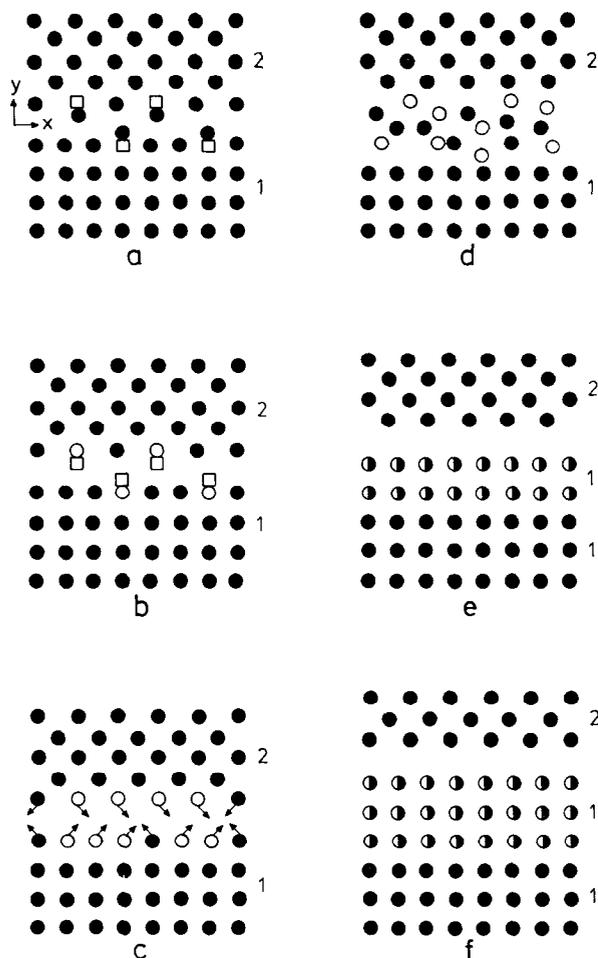


FIG. 22. Proposed atomic mechanism of the formation and growth of the W-rich phase by grain boundary diffusion between two tungsten crystallites 1 and 2; in (e) the W-rich phase grows on top of crystallite 1. Black circles: W-atoms, white circles: Cr-atoms, black-white circles; Cr- or W-atoms of the W-rich alloy, squares: vacancies in the grain boundary. See text.

the W-rich phase at a tungsten grain boundary. To this end we conceive a grain boundary as a separate phase, some atom layers wide with a high degree of imperfection and a high atomic mobility. This may be attributed to a large vacancy content in this boundary phase, which may amount to 25 per cent according to Meyering.<sup>(25)</sup> Relative to this high vacancy concentration, the presence of vacancies in the adjacent tungsten grains is ignored completely (cf. Fig. 20). In thermal equilibrium when the boundary does not move, the number of W-atoms that jump per unit time from the grain surfaces into the vacancies of the boundary equals the numbers of W-atoms which jump from the boundary and stick to these grain surfaces. However when Cr-atoms enter the boundary by normal grain boundary diffusion, the following is proposed to occur (see Fig. 22):

W-atoms from the surfaces of the crystals 1 and 2 will jump into the vacancies of the boundary (a). The resulting holes in the grain surfaces will then be filled by the more mobile Cr-atoms (b). These Cr-atoms however cannot penetrate the tungsten grains by lattice diffusion (cf. Fig. 20), because these grains cannot supply vacancies quickly enough. Instead the Cr-surface atoms are so mobile that they can easily jump back into the boundary (c) and consequently "belong" kinetically more to the boundary phase than to the tungsten crystallites, which therefore remain essentially pure (cf. Fig. 20). W-atoms from a next plane in the grains will then also come in a position to jump into the boundary vacancies. As a result the grain boundary "broadens" slightly, by which it increases however its interface energy (d). This situation can be considered as a fluctuation or an activated state, which has to be surpassed in order to nucleate a W-rich phase as a crystallized layer, epitaxially for example to crystal 1(e). When in this way from each tungsten grain one atom layer has been "dissolved" by the vacancies and an equal amount of grain boundary material (W-atoms and Cr-atoms) has been deposited in the form of a recrystallized alloy phase on top of the lower crystal 1, the grain boundary actually has moved one atom layer upwards (e). This process can now continue, whereby W-atoms from the surface of grain 2 are "distilled" together with Cr-atoms to the opposite surface of the boundary (f). In this way the grain boundary continues to move upwards, while remaining a short-circuit for supply of Cr-atoms. The W-rich phase grows by a combination of grain boundary diffusion and motion. Because of the very rapid chromium diffusion along the boundary in the horizontal  $x$ -direction (Fig. 22), the composition in the boundary will change rather slowly with increasing distance from the phase interface. Consequently the composition of the deposited layer, which is assumed to be in thermodynamic equilibrium with the Cr-rich boundary phase, will change correspondingly slowly. In the  $y$ -direction (parallel to the interface) the composition of the W-rich phase at a given  $x$ -distance will be practically constant.

In the above description it has been assumed that the W-rich phase crystallizes with the orientation of one of the tungsten grains. If the new phase were to be deposited in parallel orientation to the adjacent chromium grain, the grain boundary would be "split" and the W-rich phase would grow at the expense of both tungsten grains, i.e. as well in the  $+y$ , as in the  $-y$  direction. The mechanism of growth is for the rest essentially the same as pictured in Fig. 22.

The question arises as to what factors determine the direction of the boundary motion. It was observed that the growth of the W-rich phase can take place in different directions from separate sites at the same boundary. Probably the curvature of the boundary is a determining factor as in the case of grain growth during recrystallization.<sup>(26)</sup> On the other hand, according to Gleiter<sup>(27)</sup> the "structure" of a grain boundary is in general asymmetric, the surfaces of both grains being faceted planes of highest packing density. The number of atomic steps then differs at both sides of the boundary. It is therefore likely that the grain with the fewest steps at its surface grows at the expense of the opposite grain. On a microscopic scale it is also likely that the "structure" of a grain boundary differs from place to place, due to microscopic curvatures, the presence of impurities or dislocations which emerge from the grains. It is not unlikely that the nucleation of the W-rich phase takes place where dislocations impinge on the grain boundary, as has been proposed for the formation of the "etch pits" at the surface of tungsten single crystals (see Fig. 12).

In analogy with the mechanism of discontinuous decomposition, and in view of the discontinuous character of the formation of the W-rich phase at a grain boundary, one might describe the proposed process, in which grain boundary diffusion, reaction in and motion of the boundary cooperate, by the general term "discontinuous" diffusion. It would be interesting to investigate whether this form of diffusion occurs more generally. According to our model it would take place in a binary system, when the components differ appreciably in atomic mobility, at the grain boundaries of the less mobile metal.

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