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THE STRUCTURE OF Ni/MgO INTERFACES

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Abstract. Polycrystalline Ni has been solid state welded onto the (001) surface of MgO in vacuum, and the phase-boundary viewed face-on as well as edge-on in the transmission electron microscope. The extent of interdiffusion has been determined by energy dispersive X-ray micronanalysis, and conventional TEM has been used to study the possible formation of new phases, the possible presence of misfit dislocations and the orientation relationship between the Ni and the MgO. The theoretical misfit dislocation structures were also calculated using the O-lattice theory.

Introduction. A solid state bonded polycrystalline Ni/(001)MgO system was chosen as a model system for microstructural studies of metal-ceramic phase boundaries and the work complements previous studies on Au/MgO boundaries\(^{1,2}\). Ni and MgO were chosen partly because of their simple fcc structures, with MgO having a NaCl structure. This implies that the application of theoretical models and the interpretation of TEM images are greatly simplified. Furthermore, the surface and phase-boundaries of Ni have been reported to have the ability of self-clean \(^{2}/3\) which should contribute towards a "clean" Ni/MgO phase-boundary. The structural mismatch of the system is rather large, with a\(_{Ni} = 3.52\text{Å}\) and a\(_{MgO} = 4.21\text{Å}\). The thermal expansion coefficients of Ni and MgO are approximately the same (13.3·10\(^{-6}\)K\(^{-1}\) and 13.6·10\(^{-6}\)K\(^{-1}\), respectively), which means that the risk of debonding due to thermal expansion mismatch is greatly reduced.

Ni of 99.9% purity and (001)MgO single crystals of 99.99% purity were used. The main impurities of the latter are 30ppm CaO, 30ppm Al\(_2\)O\(_3\), 10ppm TiO\(_2\), 15 ppm SiO\(_2\) and <20ppm ZrO\(_2\). The (001)MgO surface is a very stable one (surface energy = 1.2 Jm\(^{-2}\)) and the surface structure is to a very good approximation identical to a truncation of the bulk structure (rumpling = 5 pm)\(^{1/3}\).

Experimental. Prior to bonding the MgO and Ni samples were polished to optical flatness and thoroughly cleaned in an ultrasonic acetone bath. The couple was then placed into a vacuum chamber at 10\(^{-3}\)MPa and induction heated. Two couples were solid state bonded at 1300\(^{0}\)C and...
1350°C (Ni melts at 1453°C), respectively, for a period of 2h and with an applied bonding pressure of 12MPa. TEM specimens were prepared in a conventional manner for edge-on as well as face-on viewing of the phase-boundary.

Observations. Fig 1 shows a typical weak-beam image of the face-on foil (the Ni and MgO lie on top of each other). Such images did not reveal the presence of misfit dislocations. Steps or ledges, however, were observed as a result of plastic deformation (slip) in the MgO crystal. The observations were consistent with the \text{\{110\}, \langle110\rangle} slip system of MgO.

![Weak beam dark-field image viewing the boundary face-on.](image)

Fig. 2 shows the diffraction pattern obtained from the same foil. The \text{\langle011\rangle} MgO and \text{\langle011\rangle} Ni planes define the boundary contact planes, and within these planes, the \text{\{110\}} MgO and \text{\{211\}} Ni directions are parallel, and so are the MgO \text{\{110\}} and \text{\{111\}} Ni directions.

In Fig. 2 additional reflections are seen which can be indexed as a NiO \text{\langle121\rangle} zone axis pattern. The NiO has been formed so that \text{\{111\}}NiO is parallel to \text{\{100\}}Ni and \text{\{011\}}Ni is parallel to \text{\{101\}}NiO. The dark-field imaging (Fig. 3) shows that the NiO has been formed as small crystallites (approximately 10nm) rather than a continuous layer. The NiO crystals are also found in the MgO but with a lower density than in the Ni.

Fig. 4 shows a typical image of the edge-on foil. From the diffraction pattern of this specimen (Fig. 5) it is seen that the \text{\langle001\rangle} MgO and \text{\langle021\rangle} Ni planes define the boundary contact planes, and that within these planes the \text{\{100\}} MgO direction is parallel to the \text{\{100\}} Ni direction, and the \text{\{010\}} MgO direction is approximately parallel to the \text{\{012\}} Ni direction. No NiO reflections can be seen in this diffraction pattern. The reason for this is probably that the NiO has been formed in a very narrow region immediately next to the boundary so that the total volume of the NiO in the edge-on foil is too small for any appreciable diffraction intensity to be produced.

From the edge-on foils the diffusion profiles shown in Fig. 6 were obtained. The positional error bars represent the sum of the electron probe size, relative probe drift during spectrum acquisition, and electron beam broadening within the specimen. It is seen from these profiles that the region of interatomic mixing of Ni and Mg is very narrow (<40nm).

Discussion. The boundary reaction zone (region of interatomic mixing and new phase formation) is limited to a distance within 20 nm of the boundary. The possibility that prior to bonding the grains of the polycrystal Ni were placed accidently into the simple
Fig. 2. a) Original diffraction pattern from the Ni+MgO region of fig.1. The boundary was oriented exactly face-on. b) shows that this is a superposition of [001]MgO (white lines), [011]Ni (···) and [121]NiO (---) zone axis patterns. The construction outside the original pattern shows that the [110]MgO and [211]Ni directions are parallel.

Fig. 3. NiO dark-field image. In the upper left half the MgO and Ni lie on top of each other, and in the lower right half only the MgO and NiO phases are present.

Fig. 4. Typical image of the edge-on foil.
Fiq. 5. Selected area diffraction from the boundary region of fig. 4. The boundary was oriented exactly edge-on and a superposition of Ni (broken dark lines) and MgO (white lines) [100] zone axis patterns was obtained. The (001)MgO and (021)Ni planes define boundary contact planes.

Note that no NiO reflections were observed.

Fiq. 6. The energy dispersive x-ray (EDX) interdiffusion profiles of Ni and Mg. x is the distance from the boundary.

orientations shown in figs. 2 and 5 is considered highly unlikely. Hence, the observed orientation relationships between the Ni and MgO is probably a result of some nucleation and recrystallization process of Ni, initiating at the phase-boundary. It is interesting to compare these preferred low energy orientations with those observed during epitaxial growth /4/. Such studies confirm the tendency of (001)MgO and (011)Ni to define the boundary contact planes. During epitaxial growth, however, the [211]Ni direction is parallel to the [100]MgO direction, while after solid state bonding it is parallel to the [110] MgO direction. The simple cube-cube orientation relationship has occasionally been observed during epitaxial growth, but not after solid state bonding.

The theoretical structural misfit dislocations for the two preferred orientations can be derived from the 0-lattice theory /5/ as follows. Fig. 7 shows how the least distorted unit cell ($X_1$), (where $i = 1,2$ or 3) of the (001), (021) and (011) fcc planes can be described by the following vector matrices:

$$X_1 = \frac{a'}{2} \begin{bmatrix} 1 & 1 \\ 1 & -1 \end{bmatrix}, \quad X_2 = a'' \begin{bmatrix} 1 & 0 \\ 0 & \sqrt{5} \end{bmatrix} \quad \text{and} \quad X_3 = a'' \begin{bmatrix} 1 & 0 \\ 0 & 1/\sqrt{2} \end{bmatrix}$$
The structures of a) the (001) fcc, b) the (011) fcc and c) the (210) fcc atomic planes. The broken lines define the least distorted primitive unit cells.

respectively, were $a'$ is the MgO lattice constant and $a''$ is the Ni lattice constant. The points of good fit within the boundary $X_0$ is obtained from the matrix equation

$$X_0 = \left( I - A^{-1} \right)^{-1} X_1$$  

where $I$ is a unit matrix and $A$ is the product of a distortion matrix, $D$, which distorts the MgO lattice into the shape and size of the Ni lattice (i.e. $D X_j = X_j$ or $D = X^{-1} X_j$, where $j = 2$ or $3$) and a rotation matrix $R$ which rotates the distorted MgO lattice into the orientation of the Ni lattice.

For the (001)MgO/(011)Ni boundary the following expression is obtained for $A$:

$$A = D \cdot R = a''/a' \begin{bmatrix} 1 & 1 \\ 1/\sqrt{2} & -1/\sqrt{2} \end{bmatrix} \begin{bmatrix} \cos\theta & -\sin\theta \\ \sin\theta & \cos\theta \end{bmatrix}$$

where the last term is the normal expression for the rotation matrix. The value for $\theta$ is obtained from the observed orientation relationship (figs.2 and 5) and $\theta$ equals 97° for the (001)MgO/(011)Ni boundary. Solving eqn. 1 then yields

Fig. 7. The structures of a) the (001) fcc, b) the (011) fcc and c) the (210) fcc atomic planes.

Fig. 8. The O-lattice and dislocation structures of a) the (001)MgO/(011)Ni boundary and b) the (001)MgO/(021)Ni boundary.
This 0-lattice is plotted in fig. 8a.

Using the same procedure as above, the following expression is obtained for the 0-lattice of the (001)MgO/(021)Ni boundary:

$\mathbf{x}_0 = \begin{bmatrix} 1.83 & 0.89 \\ 0.56 & 0.11 \end{bmatrix}$ nm.

This 0-lattice is plotted out in fig. 8b.

The line vectors of the theoretical misfit dislocations are predicted to run along the directions of maximum misfit. These are obtained by constructing a Wigner-Seitz cell around the 0-lattice points. Fig. 8 shows that the segment lengths of such dislocations would vary from a fraction of a nm up to a few nm. Clearly, it would be difficult to observe such dislocation patterns by weak-beam imaging where the resolution limit is around 2 nm.

Summary. The studies of the solid state bonded Ni/MgO boundaries can be summarized as follows:

1) The region of the interatomic mixing of Ni and Mg as observed by EDXS is less than 40 nm.

2) Ni seems to recrystallize into preferred low energy orientations defined by:
   a) (001)MgO parallel to (021)Ni, with [100] MgO parallel to [100] Ni and [010] MgO parallel to [012] Ni,

3) The theoretical (0-lattice) misfit dislocation segment lengths are of the order of a fraction to a few nm, and is beyond the resolution of weak-beam imaging.

4) Small crystallites (approximately 10 nm) of NiO are found within a narrow region (approximately 20 nm) of the boundary region.

5) The orientation relationship between the Ni and NiO is such that (121)NiO is parallel to (011)Ni, (111)NiO is parallel to (100)Ni and (101)NiO is parallel to (001)Ni.

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