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The complete identity of a second-phase precipitate detected by transmission electron microscopy in combustion-synthesized NiAl was established. The crystal structure, including the point group, the space group and the lattice parameters, was determined by convergent and selected-area electron diffraction techniques. Energy dispersive X-ray spectroscopy was used for the determination of the chemical composition. Analysis established the phase to be the solid solution of NiO in Al_2O_3 and presented evidence of the hitherto unreported room-temperature solubility.

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1. Introduction

Self-propagating high-temperature synthesis (SHS), or combustion synthesis, is a novel technique for processing advanced materials, including ceramics, intermetallics and composites. It is based on efficient utilization of the exothermicity of a chemical reaction. The details of this method are discussed in a number of recent reviews (Merzhanov, 1990; Munir & Anselmi-Tamburini, 1989; Moore & Feng, 1995; Varma *et al.*, 1998). This process has many attractive attributes, including the desired control of product stoichiometry and improved purity of the product. These advantages have made SHS an ideal alternative to conventional techniques for the synthesis of NiAl, which has a very high heat of reaction. Single-phase NiAl of the desired chemistry can be prepared in a single step by SHS by utilizing its heat of reaction.

Normally, the combustion-synthesized product has a better purity as a result of the removal of volatiles. However, during the course of an investigation of the combustion synthesis of NiAl from a mixture of the component powders, a second-phase precipitate containing Al, Ni and O was observed to be sparsely distributed in the matrix of B2 NiAl. This phase was detected only by transmission electron microscopy (TEM) and was not observed in either an optical microscope or by X-ray diffraction because of the small size and amount of the precipitates.

There are five ternary oxides in the Al–Ni–O system (Table 1) (Petzow & Effenberg, 1993). The primary solubility of NiO in Al_2O_3 is not very high and there is no report available in the literature about the solubility at room temperature (Table 2). The precipitate described herein was found to have a nickel concentration of 0.58 at.%. Moreover, its diffraction patterns could not be indexed in terms of either pure Al_2O_3 or any other ternary oxide listed in Table 1. In view of this, the present study was aimed at ascertaining the complete identity of the phase, in terms of both its chemistry and the crystal structure. The chemical composition as indicated above was

determined by using energy dispersive X-ray spectrometry (EDS) combined with the TEM since the precipitates were too small in size to be suitable for any other more accurate spectroscopic technique, like EPMA (electron probe microanalysis). The crystal structure, including point group, lattice parameter and space group, was determined by electron diffraction using both convergent and selected-area electron diffraction.

2. Experiments

The samples were prepared from mixtures of powders of nickel and aluminium by the SHS technique in thermal explosion mode, which gave rise to a combustion temperature (T_c) exceeding the melting point of NiAl. The synthesis was carried out both under vacuum and in argon atmosphere with three different particle sizes of nickel (10.94, 110.83 and 129.57 μm) and one particular particle size of aluminium (41.94 μm). Specimens for TEM were prepared by cutting discs, of 3 mm diameter, of the synthesized product, followed by dimpling and ion-milling. Ion-milled samples were subsequently jet-thinned to remove the ion-damaged areas. Specimens were made from the products derived from all three different particle sizes of nickel. The camera length of the transmission electron microscope was calibrated by using MoO_3 crystals grown on a copper grid.

3. Results

3.1. Microstructure

The microstructure comprised B2 NiAl matrix and precipitates of a second phase. The precipitates were found both in the grain boundaries and within the interior of the grains. In some cases, clusters of precipitates were also observed. The sizes of the precipitates, as measured from the transmission electron micrographs, without any stereological correction,

Table 1
Structure and composition of Al₂O₃ and other ternary oxides of the Al–Ni system (Petzow & Effenberg, 1993).

	Compound					
	Al ₂ O ₃	NiAl ₂ O ₄	9Al ₂ O ₃ .2NiO	NiO.13Al ₂ O ₃	NiO.16Al ₂ O ₃	2Al ₂ O ₃ .5NiO.18H ₂ O
System	Rhombohedral	Cubic	Monoclinic	Tetragonal	Monoclinic	Hexagonal
Space group	<i>R</i> $\bar{3}c$	<i>Fd</i> 3 <i>m</i>	–	–	–	–
O (at.%)	60	57.14	59.18	59.7	59.75	39.2
Al (at.%)	40	28.57	36.73	38.8	39.02	5.4
Ni (at.%)	0	14.28	4.08	1.49	1.22	6.75

Table 2
Solubility of NiO in Al₂O₃ (Petzow & Effenberg, 1993).

Temperature (K)	Solubility (mol% NiO, at.% Ni)
1973	2.7, 0.54
1473–1273	1.8, 0.36
Room temperature	Unreported

were found to be within a range of 0.33 to 1.83 μm . This was a measure of the maximum possible length of the precipitates. The precipitates showed a variety of shapes that included nearly spherical, cuboidal, ellipsoidal and oblate forms. The size, shape and distribution of the precipitates were not found to change with the change in nickel particle size. Fig. 1 illustrates some of these aspects.

3.2. EDS analysis

Table 3 displays a typical data set obtained by EDS analysis by a single precipitate from a specimen obtained using fine Ni particles (10.94 μm). Similar results were obtained with the specimens prepared with coarse Ni particles (110.83 and 129.57 μm). A number of such precipitates were analysed. Fig. 2 shows a typical EDS spectrum obtained from the precipitate. Evidently, this phase was very rich in oxygen and had very little nickel in it. EPMA of the NiAl matrix was used for the *k*-factor correction for Ni/Al and the theoretical values of the *k* factor given by the Zaluzec model (Zaluzec, 1979) for O/Al and O/Ni were used in the absence of any experimental parameter. By coincidence, the Ni/Al *k* factor determined experimentally was found to match very closely the theoretical value predicted by the Zaluzec model. The composition thus corrected was 70.08 at.% O, 29.34 at.% Al and 0.58 at.% Ni, and was not found to match that of any of the reported ternary oxides listed in Table 1.

3.3. Point-group determination

Convergent-beam electron diffraction (CBED) was used to determine the point group. In order to do this, it is necessary to select a high-symmetry zone axis. Figs. 3 and 4 show the CBED analysis of a zone that displays sixfold symmetry in a selected-area diffraction (SAD) pattern (Fig. 3*a*, inset). Both the whole pattern (WP) (Fig. 3*a*) and the bright-field pattern (BP) (Fig. 3*b*) in that zone axis showed the presence of 3*m_v* symmetry, as depicted schematically in Fig. 3(*c*). This mirror is denoted as *m_v* to show that it is perpendicular to the specimen surface (Tanaka & Terauchi, 1985). As demonstrated by the

Figure 1
Micrographs showing the precipitates (arrows) both (*a*) within the grain and (*b*) at the grain boundary.

schematics (Fig. 4), it is apparent that the dark-field pattern (DP) had a mirror symmetry *m₂*, a situation in which the mirror was perpendicular to the reflection vector, and the +*G* and –*G* conditions were related by the 2_{*R*}*m_v* symmetry. Now, by referring to the work of Buxton *et al.* (1976, Table 2 therein), it could be seen that only two diffraction groups,

Table 3

A typical set of EDS data from a single precipitate.

	Composition (at.%) at positions				
	1	2	3	4	5
O	71.8	70.5	67.6	71.2	69.3
Al	27.6	29.0	31.7	28.3	30.1
Ni	0.6	0.5	0.7	0.5	0.6

namely $3m$ and 6_Rmm_R were consistent with the combination of WP symmetry $3m_v$ and BP symmetry $3m_v$. However, when DP symmetries were taken into account, it was found that only the 6_Rmm_R diffraction group had the $\pm G$ symmetry of 2_Rm_v and thus the possibility of a $3m$ diffraction group was ruled

Figure 2

EDS spectrum of the second-phase precipitates.

Figure 3

Zone-axis patterns (ZAPs) showing (a) the symmetry in WP (corresponding SAD pattern is inset) and (b) the symmetry in BP. A schematic representation of the symmetry is also presented (c).

Figure 4

Dark-field symmetries and their schematic representations.

out. The work of Buxton *et al.* (1976, Table 3 therein) also shows that only two possible point groups, $\bar{3}m$ (rhombohedral) and $m\bar{3}m$ (cubic), correspond to the diffraction group 6_Rmm_R . Table 4 herein represents this.

If we were dealing with the cubic structure, this particular zone axis (Fig. 3a) would correspond to $\langle 111 \rangle$. In this case, if the specimen were tilted about the reciprocal vector by an angle of 54.73° and about the reciprocal vector $[101]^*$ by an angle of 35.26° , then the $\langle 100 \rangle$ and $\langle 110 \rangle$ zones should be arrived at respectively. This point is manifested clearly by the standard stereographic triangle of B2 NiAl along with the SAD patterns (Fig. 5) generated accordingly. A tilting exercise using the cubic analogy was performed and the zone-axis patterns (ZAP) are shown in Fig. 6. The similarity of these patterns to the $\langle 110 \rangle$ and $\langle 100 \rangle$ ZAPs of the cubic structure is striking. However, even though the patterns are similar, the ZAP shown in Fig. 6(b) does not show the fourfold symmetry. Instead, the angle between the $01\bar{1}2$ and $10\bar{1}2$ spots was found to be 87° (the indexing of the patterns is discussed in the following paragraph). Thus the only possible point group is the rhombohedral $\bar{3}m$. Since a rhombohedral structure can be visualized as a cubic structure stretched along the body diagonal, *i.e.* the $[111]$ direction, this angle will be the rhombohedral α angle (α_R) for the three-layer structure.

Table 4

Possible diffraction groups and point groups.

BP symmetry	WP symmetry	DP symmetry	$\pm G$ symmetry	Possible diffraction group	Possible point group
$3m_v$	$3m_v$	m_2	2_Rm_v	6_Rmm_R	$\bar{3}m$ $m\bar{3}m$

Figure 5
Standard stereographic triangle of B2 NiAl.

3.4. Lattice parameter determination

From the HOLZ rings of the CBED pattern taken in the zone $\langle 0001 \rangle$, it is possible to determine the lattice parameter of the c axis of the hexagonal basis (c_H) by using the following relationship (Williams & Carter, 1996):

$$1/H = (2/\lambda)(\lambda L/r)^2,$$

where H is the spacing of the reciprocal-lattice planes parallel to the electron beam and r is the radius of the HOLZ ring measured from the photograph (Fig. 7). As a result, the real-lattice spacing ($1/H$) parallel to the beam direction in this zone axis would give the value of c_H . Thus, the value of c_H determined from CBED (Fig. 7) was found to be 12.84 Å. The MoO_3 standard was used for calibration of the camera constant (λL) at 160 kV.

The lattice parameter a_H of the hexagonal cell was determined from the following relationship (Barrett & Massalski, 1968) using the value of c_H and the rhombohedral angle α_R :

$$\sin(\alpha_R/2) = (3/2)[3 + (c_H/a_H)^2]^{-1/2}.$$

Figure 6
SAD patterns generated by the tilting exercise.

Figure 7
CBED pattern showing the HOLZ rings that were used for lattice parameter determination.

Thus, $a_H = 4.855$ Å was obtained. The zone also contained the a axis. The value of a_H calculated from that matched well the above value.

With this information, it was possible to calculate the d spacings of the crystal. Using those d -spacing values, the SAD patterns of many other zones generated in this work could be successfully indexed. Fig. 8 shows the ZAPs of the $[01\bar{1}0]$ and $[\bar{1}2\bar{1}0]$ zones.

3.5. Space-group determination

The reciprocal lattice of the phase was constructed by using SAD patterns from the following three zones: $[0001]$, $[01\bar{1}0]$

Figure 8
SAD patterns of zone axes with their corresponding keys: (a), (b) $[01\bar{1}0]$ (double-diffracted reflections are indicated by crosses); (c), (d) $[\bar{1}2\bar{1}0]$.

Figure 9

The reciprocal lattice of the phase as deduced from the SAD patterns $[0001]$, $[01\bar{1}0]$ and $[\bar{1}2\bar{1}0]$.

and $[\bar{1}2\bar{1}0]$. Fig. 9 depicts the reciprocal lattice. Also shown is the smallest reciprocal-lattice cell that can be built within that lattice, which, in this case, is a rhombohedral one. This clearly indicates that the real-space lattice will be rhombohedral. This left us with only two possible space groups for this unknown phase: $R\bar{3}m$ or $R\bar{3}c$. However, the reflection conditions given in Table 5 were the same for both $R\bar{3}m$ and $R\bar{3}c$ except for conditions numbered 4 and 5. The $1\bar{1}01$ -type and the 0003 -type reflection are forbidden for the $R\bar{3}c$ structure. As shown in Figs. 8(c) and 8(d), the 0003 spot was missing in the $[\bar{1}2\bar{1}0]$ pattern and hence the space group was proved to be $R\bar{3}c$. It may be noted here that α - Al_2O_3 also has the same point group and space group.

4. Discussion and conclusions

Chemical analysis certainly proved that the precipitate was a compound of aluminium and oxygen containing a small amount of nickel, although the relative proportion of oxygen in the compound was not found to correspond to $\text{Al}_2\text{O}_3 + 2.85 \text{ mol\% NiO}$ (equivalent to 0.58 at.% Ni). This anomaly has arisen apparently because the theoretical values of the k factors were used for the O/Al and O/Ni combinations. The k factors, being necessarily only sensitivity factors, depend to a great extent on the actual experimental conditions. However, subsequent determination of the point group and the space group implied that the precipitate phase was essentially the solid solution of NiO in Al_2O_3 since α - Al_2O_3 also has the same point group and space group. Table 6 compares these two structures. It may be noted that there was a reduction in the c parameter and an increase in α and a . That is, the structure can be derived from the unit cell of α - Al_2O_3 by compression of its c axis, resulting in the increase of the rhombohedral angle and

Table 5

Reflection conditions of the space groups $R\bar{3}m$ and $R\bar{3}c$.

General conditions are listed; there are no extra special conditions.

	$R\bar{3}m$	$R\bar{3}c$
1	$hkl\bar{l}: -h + k + l = 3n$	$hkl\bar{l}: -h + k + l = 3n$
2	$hki0: -h + k = 3n$	$hki0: -h + k = 3n$
3	$hh2hl: l = 3n$	$hh2hl: l = 3n$
4	$h\bar{h}0l: h + l = 3n$	$h\bar{h}0l: h + l = 3n, l = 2n$
5	$000l: l = 3n$	$000l: l = 6n$
6	$h\bar{h}00: h = 3n$	$h\bar{h}00: h = 3n$

Table 6

Comparison between α - Al_2O_3 (Ishizawa *et al.*, 1980) and the precipitate.

	α - Al_2O_3	Precipitate
Point group	$\bar{3}m$	$\bar{3}m$
Space group	$R\bar{3}c$	$R\bar{3}c$
c_H (Å)	12.99	12.84
a_H (Å)	4.754	4.855
α (°), three-layer	85.68	87
α (°), six-layer	55.25	56.65

the a parameter. This would be the likely situation if a smaller atom, such as Ni, had substituted a large atom, Al, in the crystal lattice of α - Al_2O_3 . Thus, the rationalization of the comparison between the lattice parameters and the rhombohedral angles of the precipitate and α - Al_2O_3 further substantiates the view that the phase under scrutiny is a solid solution of NiO in Al_2O_3 . As far as the degree of solubility of NiO in Al_2O_3 at room temperature is concerned, the value suggested by the current EDS data is more than the maximum solubility reported earlier. If the proportion of oxygen is made to match the stoichiometry of Al_2O_3 , in which the ratio of the concentrations of aluminium to oxygen atoms is 2:3, the effective nickel concentration of the precipitate phase would increase a little further. However, the nature of the sample did not permit that experiment. In other words, though this analysis provided definite proof of the room-temperature solubility of NiO in Al_2O_3 , it could not be established quantitatively because of experimental limitations. Since the alumina-rich side of the NiO- Al_2O_3 pseudo-binary phase diagram (Petzow & Effenberg, 1993) does not show any solubility of NiO in Al_2O_3 at room temperature, further investigation needs to be carried out to resolve the issue. SHS is a non-equilibrium processing technique in which the formation of metastable and supersaturated phases is not unlikely. Since the solubility of NiO increases with temperature, there is a possibility that the observed solubility of NiO is the result of supersaturation. This likelihood is challenged by the fact that the observed solubility is more than the reported value and the fact that the rates of cooling in the current experiments were not sufficiently high. However, it is also probable that the observed precipitate is a new metastable phase.

The reason for the formation of this oxide must lie in the surface oxygen of the metal powders because the reactions

were always carried out either under vacuum or in an inert atmosphere. The microscopy observation indicated that the particle size of the nickel powders did not show any influence on either the size of the precipitates or their total volume percent. Also, in all the cases the precipitate volume percent was below the detection level of X-ray diffraction. It is possible that the oxygen on the surface of aluminium is responsible for the generation of the oxide. This is probable because (i) the same particle size of aluminium was used for all the experiments and (ii) the amount and size of the precipitates were insensitive to the variation of nickel particle size.

This study proffers one more issue which is important from the point of view of the purity of combustion-synthesized products: though combustion synthesis can definitely reduce the volatile and gaseous impurity level, the possibility of forming oxide precipitates of one or more components cannot be totally ruled out, especially in the case of intermetallic synthesis in which metallic powders are handled.

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