Interaction between liquid aluminum and NiO single crystals

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The wetting behavior of NiO single crystal by liquid aluminum has been studied by the sessile drop method under vacuum at 973–1273 K for 2 h. Optical microscopy, SEM, EDS and X-ray analysis were applied to characterize the structure and chemistry of solidified cross-sectioned sessile drop couples. Under tested conditions, molten Al wets and reacts with NiO to form Al_2O_3 and Ni. This leads to alloying of the initially pure Al drop with Ni to the hypereutectic composition and to the formation of a thick reaction product region inside the NiO substrate, whose structure presents interpenetrated networks of fine alumina precipitates and an Al–Ni matrix. After solidification the Al–Ni matrix and the drop have the same phase composition, which is in agreement with Al–Ni phase diagram, showing the formation of Al_3Ni at $T < 1128$ K and Al_3Ni_2 at 1128 K $< T < 1406$ K. The strong reactivity of Al/NiO couples, accompanied with the drop deformation, fragmentation of the reaction product region and development of a crater under the drop, contributes to the perturbation of the triple line and to the formation of apparent contact angles at 1073–1273 K. This leads to unusual changes of measured contact angles with temperature, decreasing from 84° at 973 K to 36° at 1073 K, and then increasing to 75° at 1273 K, while structural analysis suggests complete wetting at 1073 K. © *2005 Springer Science + Business Media, Inc.*

1. Introduction

Metal and ceramic matrix composites of Al-Al_2O_3 and Al_xMe_y–Al_2O_3 systems (Al_xMe_y—intermetallic phase) can be produced *in situ* by liquid reactive processing using oxy-redox replacement reactions between molten aluminum and reactive oxides (MeO) by means of vortex casting [1], reactive metal infiltration of porous ceramic preforms [2] or by reactive metal penetration of dense ceramics [3–6]. Independent of the specific process involved, wettability and reactivity of the Al/MeO couples are required.

Thermodynamic analysis given in [4–6] suggests that among different Al/MeO couples, Al/NiO is a candidate for *in situ* liquid reactive methods as a general route to composite synthesis, with the prospect for near net-shape processing even at a temperature close to the melting point of Al. There are no data on wetting properties of the Al/NiO system in open literature. Loehman *et al.* [5] reported unsuccessful attempts to infiltrate polycrystalline NiO by liquid Al at 1173–1473 K in an atmosphere of Ti-gettered Ar. The authors suggested that this disagreement with thermodynamic predictions might be explained by a lack of wettability

in the Al/NiO system. Fahrenholtz *et al.* [6] reported that a much higher temperature of 1673 K was needed to produce NiAl−Al_2O_3 and Ni_3Al−Al_2O_3 composites from mixtures of Al and NiO or $NiAl_2O_4$ powders by reactive metal penetration for 2 hours in ultra high purity argon gettered with titanium at temperatures above over 973 K. On the contrary, the observations of the behavior of NiO powder as well as oxidized Ni-coated ceramic powders (alumina, graphite) during their incorporation into Al melt in vortex casting suggest that molten Al should wet NiO [7]. In this paper wettability and reactivity of the Al/NiO system has been examined.

2. Experimental procedure

The wetting behavior of NiO single crystal by liquid aluminum (99.9999) has been studied by the sessile drop method at a temperature of 973–1273 K for 2 h in vacuum (3–8×10^{-4} Pa) using contact heating of the Al/NiO substrate couples to the test temperature with a rate of 10 K/min. The experimental set up was operated with a turbo-molecular pump and Mo heater surrounded with Mo heat shields. NiO single crystals
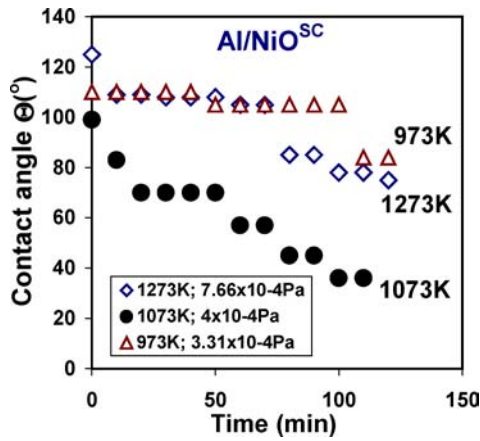
Figure 1 Effect of temperature on wettability kinetics in Al/NiO.

were produced by Verneuila's method. The tests were done on the (100) NiO surface of average roughness $R_a \approx 2$ nm. Directly before wettability tests the Al samples were cleaned mechanically and then ultrasonically in acetone together with the NiO substrates. After wettability tests the sessile drop samples were cooled at a rate of 10 K/min, cross-sectioned and polished with a diamond suspension for microstructural examinations using optical microscopy under polarized light, Scanning Electron Microscopy (SEM), X-ray Electron Spectroscopy (EDS) and X-Ray Diffraction (XRD). No additional treatments (e.g., etching, deposition of conductive thin films) of the samples were used in all examinations.

3. Results and discussion

Liquid aluminum wets NiO and non-wetting-to-wetting transition (the contact angle $\theta = 90°$) takes place after about 100, 5 and 70 min at 973, 1273 and 1073 K, respectively. The value of contact angle after 2 h tests decreases with temperature from $\theta^{973 \text{ K}} = 84°$ to $\theta^{1073 \text{ K}} = 36°$ (Fig. 1). A further increase in temperature results in a larger contact angle of $\theta^{1273 \text{ K}} = 75°$. An explanation of the unusual change in contact angle values with temperature was found from microstructural analysis of the sessile drop samples, suggesting that the measured values correspond to the apparent contact angles θ^* (Table I). The results clearly demonstrate that in the temperature range of 973–1237 K there is a strong interaction between molten aluminum and NiO leading to two phenomena: (1) the phase transformation of initially pure Al drop to Al–Ni alloy, in which the amount of Ni significantly increases with temperature of the sessile drop experiment; (2) the formation of a thick reaction product region (RPR) in the substrate. The RPR has an interpenetrating metal-ceramic composite microstructure composed of very fine ceramic particles surrounded by an Al-rich metallic network, whose phase composition corresponds to that of the drop.

SEM analysis of the samples after 953 K test (Fig. 2, Table I) shows a hypereutectic composition of the initially pure Al drop. It is composed of the (Al + Al_3Ni) eutectic and about 10 vol% primary Al_3Ni phase, solidified in the form of large crystals both inside the drop and at the interface. In this sample, the RPR has a different thickness along the interface (about 200 μm
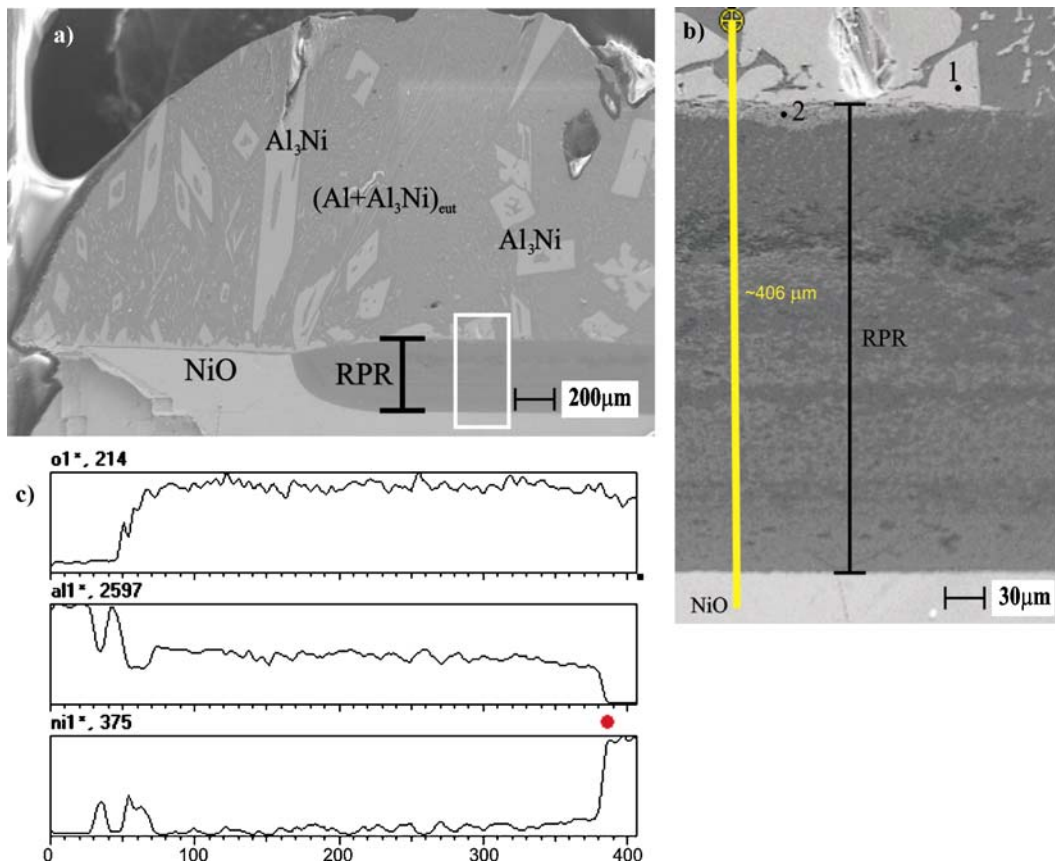

Figure 2 SEM analysis of Al/NiO couple (973 K, 2 h); (a, b) interface views; (c) distribution of O, Al and Ni along white line as shown in (b).

TABLE I Results of wettability tests and structural analysis

Conditions of wettability tests	$\theta(°)$	Phases formed	Point phase analysis				
			Point	Al (at%)	Ni (at%)	O (at%)	Phase composition
973 K, 120 min	84	Al_3Ni, Al_2O_3	**1** (Fig. 2b)	75.17	24.83	–	Al_3Ni
			2 (Fig. 2b)	68.18	10.22	22.60	Al_3Ni, Al_2O_3 + Al(Ni)
1073 K, 120 min	36[a]	Al_3Ni, Al_2O_3	**3** (Fig. 3f)	73.24	26.76	–	Al_3Ni
			4 (Fig. 3f)	43.51	–	56.49	Al_2O_3
1273 K, 120 min	75[a]	Al_3Ni, Al_3Ni_2, Al_2O_3	**5** (Fig. 5)	71.22	28.78	–	Al_3Ni
			6 (Fig. 5)	56.71	43.29	–	Al_3Ni_2

[a]The values correspond to the apparent contact angles θ^*.
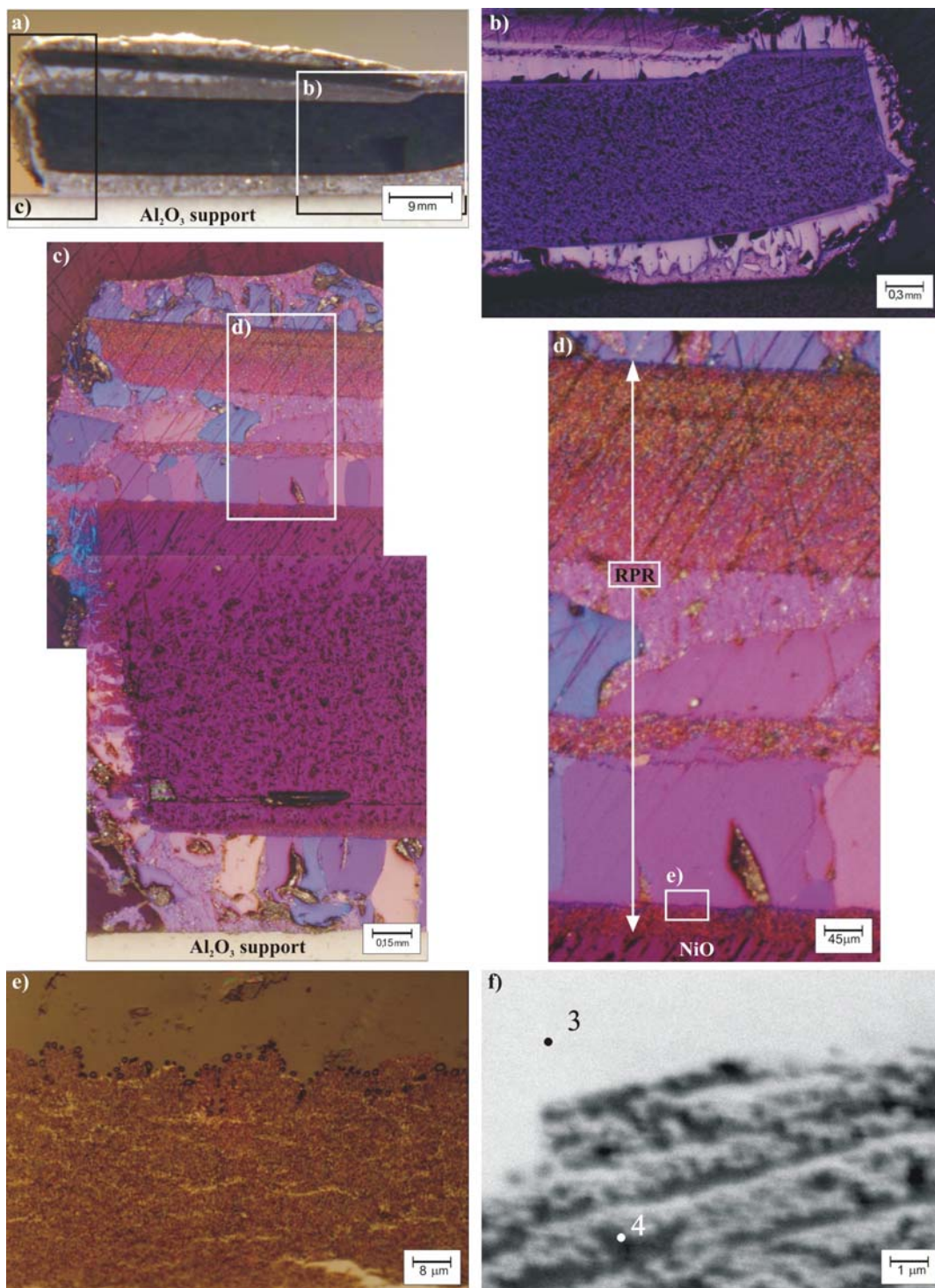

Figure 3 (a–e) Optical micrographs of Al/NiO couple (1073 K, 2 h) under different magnifications of the regions as marked; (f) SEM image of the drop/RPR interface shown in (e).
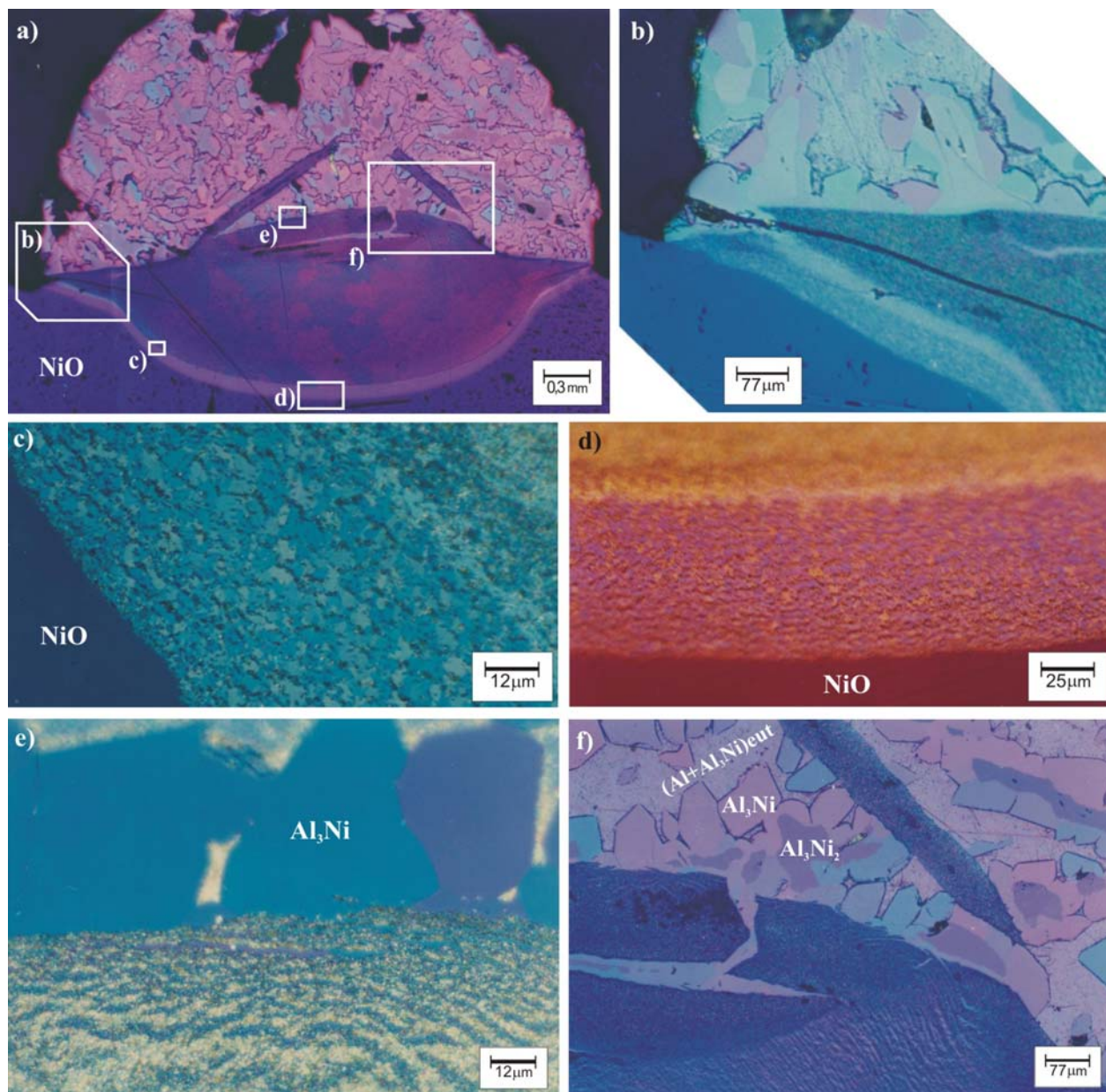
Figure 4 Optical micrographs of Al/NiO structure (1273 K, 2 h) under different magnification taken from the regions as marked.

in the center of the sample and only 5 μm at the periphery of the drop) and an inhomogeneous microstructure. The RPR region corresponding to the central part of the sample has two different layers, easily distinguished by SEM (Fig. 2b): the drop-side (light-gray layer) has a more course microstructure compared to the denser substrate-side (darker layer). However, the distribution of Al, Ni and O across the layers characterized by EDS (Fig. 2c) does not show a significant difference in chemical composition between these layers suggesting that their structural dissimilarity is related to different degrees of dispersion of the contributing phases.

During the 1073 K test, the Al drop completely spreads along the NiO surface. Structural analysis of this sample has shown that all faces of the NiO substrate are covered with a metallic layer (Fig. 3a), even its bottom surface placed on the alumina support (Fig. 3b and c). It suggests complete wetting, i.e., the true contact angle tends to 0°. On the other hand, the position of the triple line is not well distinguished due to deformation of the drop caused by the formation of a crater under

it and by detachment of some layers of RPR accompanied with their movement inside the drop, all contributing to the apparent measured angle. The upper thin layer of the drop, optically free of RPR, is mainly composed of large Al_3Ni grains surrounded by a small amount of the $(Al + Al_3Ni)$ eutectic (Fig. 3c). The remaining volume of the drop is intermixed with fragmented RPR of layered and less condensed microstructure compared to its other regions (Fig. 3d). Also in that sample the RPR contains highly dispersed particles, whose chemical composition suggests the formation of Al_2O_3 (Fig. 3e and f).

For 1273 test (Fig. 4), a strong interaction between the Al drop and the NiO substrate results in an apparent angle due to the development of a deep crater under the drop and a large lens-type shape of RPR, comparable to the size of the drop. SEM analysis (Fig. 5) shows that about 20 vol% of the drop is composed of a phase, characterized by a light contrast and irregular shape, whose chemical composition corresponds to Al_3Ni_2. Each grain of Al_3Ni_2 phase is surrounded
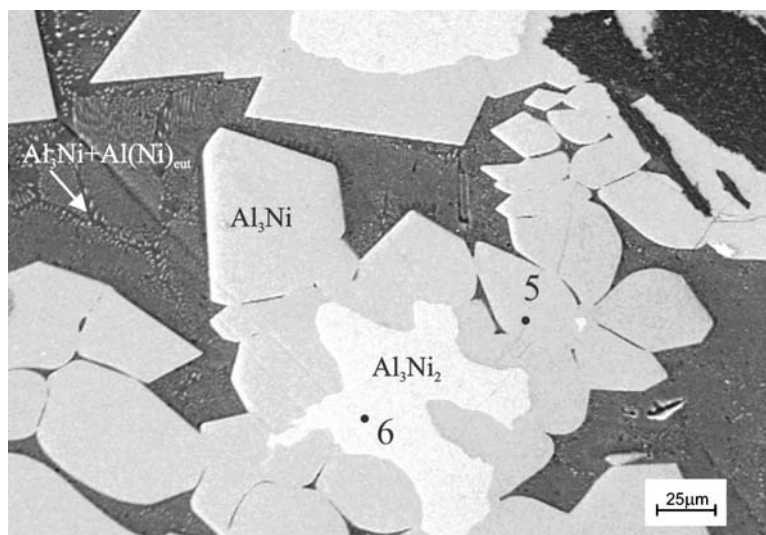
Figure 5 SEM image of the drop in the Al/NiO couple produced at 1273 K.

by the Al_3Ni phase of a gray contrast (about 40 vol%), formed during cooling due to the peritectic reaction between $L_{(Al-Ni)}$ and Al_3Ni_2 phases. The remaining area of the drop (about 40 vol%) presents the $(Al+Al_3Ni)$ eutectic. Detailed microstructural characterization by optical microscopy shows a layered structure of highly dispersed RPR and its fragmentation in the drop-side region accompanied with movement of large pieces of RPR into the drop (Fig. 5b–f). In this couple, contrary to the samples produced at lower temperatures, the substrate-side of RPR has two layers, well distinguished due to difference in color under optical microscope in polarized light or due to difference in grayscale on the given micrographs (Fig. 5c and d). The brighter thin layer in contact with the large RPR "lens" corresponds to a chemical composition of Al_3Ni_2. The darker substrate-side layer has a chemical composition close to AlNi. Both layers are composed of small grains reinforced with very fine precipitates recognized as Al_2O_3.

In this study the efforts in identification of the type of Al_2O_3 formed were not successful due to difficulties with TEM thin film preparation caused by the brittleness of all Al/NiO samples. Also XRD did not solve the problem because on XRD profiles the peaks corresponding to the Al_2O_3 phase could not be distinguished, due to high dispersion of Al_2O_3 precipitates, mainly of nanometer size.

Comparison of the results obtained for Al/NiO^{SC} couples with those for Al/Ni system reported by Nakae *et al.* suggests the similarity of interaction in these systems owing from the formation of the same reaction products at corresponding temperatures of wettability tests. Nakae *et al.* demonstrated that at 1173 K, wetting of both pure Ni and Al_3Ni_2 substrates by the Al–Ni alloys becomes worse with increase in Ni content in the alloy showing the contact angle of Al-30 mas% Ni alloy on Al_3Ni_2 about 125° contrary to about 22° for Al-30Ni/Ni and 8° for pure Al/Ni couples, respectively. Following these data one may suggest that at 1273 K the high reactivity in the Al/NiO system, accompanied with fast diffusion of freshly formed Ni into the Al drop, leads to alloying Al with a large amount

of Ni while interfacial reactions create new interfaces of Al–Ni/Al_3Ni_2 type, characterized by worse wetting. This process as well as drop deformation and perturbation of the triple line configuration taking place in the same time, all contribute to high values of θ^* measured at 1273 K.

4. Conclusions

The results suggest that the following interfacial replacement reaction is responsible for a good wetting in the Al/NiO couples:

$$2Al + 3NiO = Al_2O_3 + 3Ni \qquad (1)$$
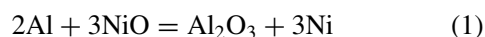
The freshly formed Ni dissolves in Al and diffuses into liquid Al drop to form Al−Ni alloy in which Ni content increases with test temperature. During cooling of the sessile drop samples produced at 973 and 1073 K, the primary large precipitates of Al_3Ni phase are formed from the liquid drop $(L \rightarrow Al_3Ni)$ while the last solidified amount presents the $(Al + Al_3Ni)_{eut}$ eutectic formed at 1113 K by the reaction:
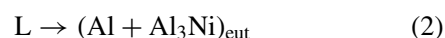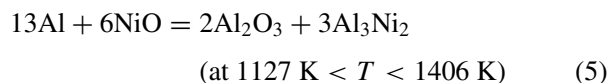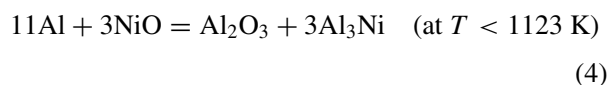
$$L \rightarrow (Al + Al_3Ni)_{eut} \qquad (2)$$

In the case of the 1273 K test, solidification of the drop starts from the formation of the Al_3Ni_2 phase $(L \rightarrow Al_3Ni_2)$. During further cooling the Al_3Ni phase is formed at 1127 K due to the peritectic reaction:

$$L + Al_3Ni_2 \rightarrow Al_3Ni \qquad (3)$$

followed by the formation of $(Al + Al_3Ni)_{eut}$ at 1113 K.

With excess of aluminum, an interaction in the Al/NiO couples can be summarized by the following reactions, depending on testing temperature:

$$11Al + 3NiO = Al_2O_3 + 3Al_3Ni \quad (\text{at } T < 1123 \text{ K})$$
$$(4)$$

$$13Al + 6NiO = 2Al_2O_3 + 3Al_3Ni_2$$
$$(\text{at } 1127 \text{ K} < T < 1406 \text{ K}) \qquad (5)$$

Interfacial reactions lead to the formation of layered structure of the reaction product region and the drop

deformation accompanied by the perturbation of the triple line configuration. All these processes become essential at about $T > 1000$ K and contribute to the formation of apparent contact angles.

The results obtained have a good agreement with thermodynamic predictions on oxy-redox replacement reactions between molten aluminum and NiO, which can be utilized for *in situ* liquid reactive synthesis of composite materials of Al-Al$_2$O$_3$ or Al$_x$Ni$_y$-Al$_2$O$_3$ systems at processing temperatures close to melting point of Al. A good wetting of NiO by Al is responsible for the easy incorporation of either NiO powder or oxidized Ni-coated ceramic particles into Al melt observed in practice during production of Al matrix composites by vortex casting.

Acknowledgment

References

1. P. C. MAITY, P. N. CHAKRABORTY and S. C. PANIGRAHI, *Mater. Lett.* **30** (1997) 147.
2. D. C. DUNAND, J. L. SOMMER and A. MORTENSEN, *A. Metall. Trans.* **24A** (1993) 2161.
3. M. C. BRESLIN, J. RINGNALA, J. SEEGER, A. L. MARASCO, G. S. DAEHN and H. L. FRASER, *Ceran. Eng. Sci. Proc.* **15**(4) (1994) 104.
4. W. LIU and U. KOSTER, *Scripta Mat.* **35**(1) (1996) 35.
5. R. E. LOEHMAN, K. EWSUK and A. P. TOMSIA, *J. Amer. Cer. Soc.* **79**(1) (1996) 27.
6. W. G. FAHRENHOLTZ, K. V. EWSUK, R. E. LOEHMAN and A. P. TOMSIA, *Met. Mater. Trans.* **27A** (1996) 2100.
7. J. SOBCZAK and N. SOBCZAK—unpublished data.
8. H. NAKAE, T. HANE and T. SUDO, *Trans. JWRI* **30** (2001) 27.