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The influence of interfacial wetting and adhesion on the formation of voids at metal-ceramic interfaces

G. LEVI, W. D. KAPLAN
Department of Materials Engineering, Technion-Israel Institute of Technology, 32000 Haifa, Israel

High temperature sessile drop experiments were conducted to evaluate the wetting (contact angle, surface/interface energies) on the basal C and prismatic A surfaces of sapphire by pure liquid Ni, and Ni alloyed with Al or S. After solidification of the drops, inspection of samples showed the presence of millimetre-sized voids at the interface between pure nickel and the basal surface of the sapphire substrate. However, no voids were found at the interfaces of pure Ni with the prismatic surface of sapphire, or at the interfaces of sapphire with Ni alloyed with 0.03at.%S or 2at.%Al, or if the pure Ni drops were significantly smaller in size. It is proposed that the voids form to release strain energy stored in the system, due to the dissimilar thermal expansion coefficients of Ni relative to sapphire. Alloying with Al and/or S retards interfacial void formation by enhancing the metal-ceramic interfacial wetting and adhesion.

1. Introduction

The properties of metal-ceramic interfaces are among the important factors limiting the potential applications of various metal-ceramic joins and composites. In this context, composites and joins of nickel and nickel-based alloys with α-Al_2O_3 are the subject of research in recent years, attributed to potential applications demanding high temperature strength and oxidation resistance [1, 2]. For example, strong bonding of α-Al_2O_3 to Ni and Ni alloys is desired, because α-Al_2O_3 scales provide protection against oxidation in high temperature environments [3, 4]. Also, the combination of α-Al_2O_3 and Ni may provide ceramic matrix or metal matrix composite materials for high temperature applications with improved mechanical properties [5–7].

The mechanical strength of a join correlates to the thermodynamic work of adhesion (W_{ad}), which is a nominal part of the interface fracture energy, Γ_{int} [8, 9]. Small changes in the thermodynamic work of adhesion may have a significant effect on the resistance to fracture [10]. As such, there has been a long tradition of trying to extract thermodynamic data from contact angles of molten metals on ceramic substrates, and then attempting to relate thermodynamic properties to the strength of the solid metal-ceramic interfaces formed by the same materials [11]. Unfortunately, no *straightforward* correlation between the thermodynamic properties of a liquid/solid metal-ceramic interface (contact angle, work of adhesion) and the mechanical strength of a join/composite formed by the same materials has been found. However, there are experimental results suggesting that the strength of alumina-FCC metal joins increases in a non-linear fashion with increasing W_{ad} [8, 12].

In this work we propose a qualitative correlation between the metal-ceramic interface thermodynamics and mechanics via analysis of interfacial voids, which form during cooling of (Ni) sessile drops on the basal surface of sapphire. In addition, we examine the influence of alloying Ni with Al or S on interfacial wetting and adhesion in Ni-Al_2O_3 systems.

2. Experimental methods

Pure Ni (99.997%), Al (99.997%) and S (99.999%) (Johnson-Matthey, Materials Technology U.K.), and pure single crystal α-Al_2O_3 (sapphire) were used as raw materials. Substrates were cut from 19 mm diameter sapphire rods, in slices of ∼1 mm, parallel to the (0001) or $(1\bar{2}10)$ plane of the crystal, i.e. the *basal* **C** or *prismatic* **A** surfaces of sapphire, respectively. The sapphire substrates were ground and polished in 1/4 μm diamond polishing media to minimise surface roughness. After polishing, the substrates were cleaned in high purity solvents in the following order: acetone, ethanol and water. To eliminate defects induced by polishing, the cleaned substrates were annealed for 2 h at 1600°C in air. Ni(2at.%Al) and

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Ni(0.03at.%S) alloys were prepared from pure Ni, Al and S in an induction furnace (12 kW, ≈300 kHz), under a protective atmosphere of argon (94%Ar + 6%H_2) in crucibles from pure alumina (99.99%, Akino, Japan). The Ni and Ni alloys were cut and polished in cubic sections weighing between 0.14 and 3.0 g.

Prior to the sessile drop wetting experiments the native oxide layer on the surface of the metal samples was removed *in-situ*, by Ar^+ ion sputtering at 1.5 kV for 1–2 min for each side of the sample, in a special section of a UHV furnace. The metal samples were then transferred to a tungsten stage located in the heater region, without breaking vacuum. The system was heated to the desired temperature, at a rate of 20°C/min under a *controlled* atmosphere by introducing pure Ar (99.999%) into the chamber at a constant flow rate of 4.0–4.2 cm^3/min, while pumping the chamber with a turbo-molecular pump. Ar was purified by passing it through a catalytic filter (AERONEX, USA) prior to entering the UHV chamber (the total capacity of the UHV chamber is ∼0.011m^3). The partial pressure of the main gases (O_2, H_2O, N_2, Ar and CO_2) was monitored *in-situ* during the experiments, using a residual gas analyser (RGA; Ferran Scientific, USA), mounted on the UHV chamber. During the actual experiments the total pressure was 10^{-1} Pa, and the partial pressure of water ranged between 10^{-6}–10^{-5} Pa. According to the producer, the catalytic filter reduces the oxygen content of the gas to ∼1 ppb, corresponding to $P(O_2)\approx 10^{-10}$ Pa for the total working pressure (10^{-1} Pa), which falls beneath the limit of detection of the RGA (10^{-7} Pa). The drop profiles were recorded *in-situ* at 1500°C over a period of ∼50 min, through a quartz window using a CCD camera (150 dot per inch resolution) connected to a computer. At the end of the actual experiments, the samples were cooled at a rate of 20°C/min to room temperature.

3. Results

The contact angle on the basal surface of sapphire and the surface energy of Ni and Ni(2at.%Al), corresponding to the working conditions from the present work, were previously reported [13]. Here, using the methods described in reference [13], these parameters were determined for Ni(0.03at.%S) on the basal surface of sapphire, and for pure Ni on the prismatic **A** surface of sapphire. Table I summarises the main wetting parameters for the studied Ni alloy-sapphire systems, measured by the authors or other researchers [13–17].

Other works reported no significant difference in the contact angle of Ni on the **C** *or* **A** surfaces of sapphire [14, 18, 19]. However, in this work a significant difference was observed (θ=112 ± 3° on **C** and θ=102 ± 3° on **A**). Although we do not rule out the effect of hysteresis, we emphasise that the measurements were conducted *in-situ*, on samples undergoing *identical* preparation and working conditions.

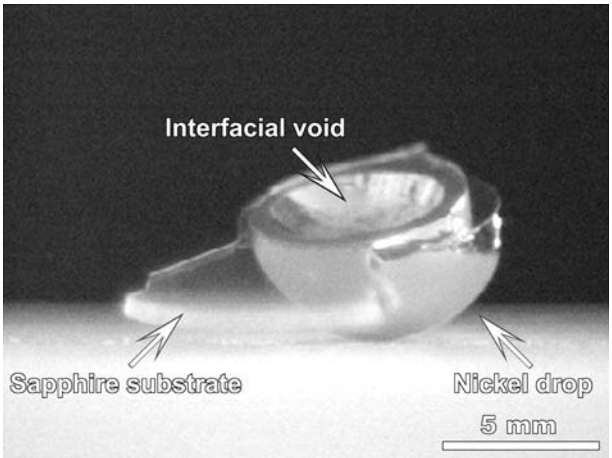

Figure 1 Photograph showing the interface of a large pure Ni sessile drop with the basal surface of a sapphire substrate, viewed through the transparent sapphire substrate, after cooling. The image shows the presence of a void in the Ni drop, at the interface. The sapphire substrate cracked during handling at room temperature. (The wetting experiment was conducted at 1500°C, $P_{TOT}=10^{-1}$ Pa, and $P(O_2)<10^{-7}$ Pa.).

To the authors' best knowledge, this is the first time that the surface energy of Ni(S) and its contact angle on alumina are being reported in the literature. However, a qualitative comparison is possible with Fe, where alloying with a similar quantity of ≈0.03at.%S results in a decrease of γ_{LV} from 1.780 to ≈1.350 J/m^2 at 1600°C [20].

Inspection of the relatively large Ni sessile drops from the wetting experiments, revealed the presence of voids at the interface made with the basal surface of the sapphire substrate (see Fig. 1). Sometimes, 2–3 smaller voids were observable, instead of one large void. In addition, the dimension of the voids increased with increasing size of the sessile drop.

In contrast, no voids were observed at interfaces with the basal surface of sapphire made by *smaller* Ni sessile drops, having a drop base diameter less than or equal to 5mm. In addition, no voids were detected for the alloyed Ni sessile drops, or at interfaces made by Ni sessile drops with the prismatic **A** surface of sapphire. Some of the substrates bonded to relatively large *Ni-alloy* drops cracked, with the main crack running parallel to the interface in the substrate. This most probably occurred during cooling. Some of the substrates bonded to relatively large *pure* Ni drops also cracked, but this occurred during handling at room temperature, and the crack was found to propagate along the interface rather than through the substrate.

The drop base diameter of the *smallest* pure Ni sessile drop found to contain a void was ≈6.5 mm, and the corresponding void base diameter was ≈2 mm, so the void volume is relatively large, representing about 1% of the volume of metal (calculated, based on the dimensions of the sample measured in cross-section).

TABLE I Wetting parameters of Ni, Ni(2at.%Al), Ni(3at.%Al) and Ni(0.03at.%S) in contact with the C-(0001) or A-($1\bar{2}10$) surface of sapphire at 1500°C ($P_{TOT}=10^{-1}$, $P(O_2)<10^{-7}$ Pa)

Sapphire substrate orientation	C	C	C	C	A
Metal alloy	Ni	Ni(2at.%Al)	Ni(3at.%Al)	Ni(0.03at.%S)	Ni
γ_{MV} [J/m^2]	$1.755 \pm 0.020^{(A)}$	$1.726 \pm 0.020^{(A)}$	$1.711 \pm 0.020^{(A)}$	$1.300 \pm 0.050^{(C)}$	$1.755 \pm 0.020^{(A)}$
θ [deg]	$112 \pm 3^{(A)}$	$100 \pm 3^{(A)}$	$95 \pm 2^{(B)}$	$95 \pm 3^{(C)}$	$102 \pm 3^{(C)}$
γ_{MS} [J/m^2]	1.657 ± 0.113	1.300 ± 0.112	1.149 ± 0.081	1.113 ± 0.092	1.485 ± 0.167
W_{ad} [J/m^2]	1.098 ± 0.113	1.426 ± 0.112	1.562 ± 0.081	1.187 ± 0.122	1.390 ± 0.114

References for data from this table: $^{(A)}$ [13]; $^{(B)}$ [14]; $^{(C)}$ this work. $\gamma_{MS}=\gamma_{SV}-\gamma_{MV}\cdot\cos\theta$ (from Young's equation). $W_{ad}=\gamma_{MV}\cdot(1+\cos\theta)$ (Young-Dupré equation). For the basal surface of sapphire $\gamma_{SV}(C)=1.000 \pm 0.020$ J/m^2 [15, 16], and extrapolated to 1500°C according to [15]). For the A prismatic plane of sapphire $\gamma_{SV}(A)\cong 1.120 \pm 0.073$ J/m^2 ([17] gives $\gamma_{SV}(A)/\gamma_{SV}(C)=1.12 \pm 0.05$ at 1600°C).

4. Discussion

Given the experimental conditions, three possible causes may account for formation of the voids; (i) inclusion of gases from the raw materials or from a reaction between the metal and the substrate; (ii) heterogeneous nucleation of the void during solidification (shrinkage); or (iii) the action of stresses due to the elastic strain induced within the system during cooling, especially at the interface.

The experiments were conducted under a relatively low pressure in the gravitational field, i.e. under conditions in which buoyancy and degassing are enhanced. Therefore it is concluded that inclusion of gases is *unlikely* to be the cause for void formation at the interface.

The thermodynamic interfacial balance $\gamma_{MV}+\gamma_{SV}<2\gamma_{MV}+\gamma_{MS}$, ($\gamma_{MS}$, γ_{SV}, γ_{MV} are the metal-substrate, substrate-vapour and metal-vapour interface energies, respectively; see Table I) suggests that formation of a shrinkage (solidification) void at the interface might be favoured versus its formation within the bulk metal. However, the experimental results from this work show that *no voids* form at the interfaces of either Ni on the **A** surface of sapphire, small Ni drops on the **C** surface, or Ni(Al) and Ni(S) on the basal surface of sapphire, produced under identical working conditions, and for which the above energetic balance is maintained. Still, one may argue that since the energy of the interface made by Ni on the basal surface of sapphire is the largest among the systems investigated in this study (see Table I), the energetic barrier for heterogeneous nucleation of solid Ni on the basal surface of sapphire is the highest, which conversely, favours formation of a void at this interface. However, this is not sufficient to explain the systematic absence of voids from the interface of small Ni drops with the **C** surface of sapphire.

Radiation is likely to favour a faster advance for the solidification front moving from the free surface than for the solidification front moving from the interface, which eventually could result in the formation of a void at the interface. However, the thermal conductivity of sapphire above 1000°C is still relatively high and there is no data indicating anisotropy of this parameter with crystallographic direction at temperatures close to the melting temperature of Ni (1453°C) (≈6 W/mK for pure alumina [21] versus ≈105 W/mK for W [22] and ≈85 W/mK for Ni (extrapolated) [22]). Thus, the sapphire substrate may convey a significant amount of heat out of the metal sessile drop during the course of solidification, under the applied working conditions. This suggests that the first (solid) Ni nuclei forms at the triple junction region of the sessile drop, where heat transfer takes place by both radiation and conduction, and heterogeneous nucleation is favoured by contact with the sapphire substrate. Next, it may be considered that nucleation of the solid phase continues along the interfaces, and proceeds towards the centre of the drop. Finally, it is reasonable to assume that for the Ni drops from this study, the last pocket(s) of liquid is more likely to solidify within the drop. In fact, close to the melting temperature, Ni has a predominantly plastic behaviour ([23]; see also Fig. 2), so that although the volume contraction during solidification of Ni is relatively high (4–5%), it is not clear whether solidification of the central region of the drop plays a role at all in the formation of voids at the Ni-sapphire interface. Hence it is concluded that formation of the void at the interface is unlikely to occur during solidification of the Ni.

In conclusion, it may be considered that formation of the void takes place at a relatively high temperature, but *after* solidification of the metal. This process would involve two main stages (i) *flawing* and *disjoining* of the interface, under the action of the elastic strain (stress), and (ii) *contraction* and *deformation* of the metal to form a void such as shown in Fig. 1. As a reinforcement, note that ΔT^*, the relative change in temperature to produce a void at the interface in *solid* Ni, with a volume of ≈1% of the metal drop, is $178<\Delta T^*<361$°C (the lower value corresponds to the free contraction of Ni; the higher value corresponds to the contraction of Ni fully constrained by alumina; also see Table II), which is consistent with the above assumption. Since sapphire contracts less than solid Ni [21, 24], the sapphire substrate may hinder the contraction of solid Ni during cooling, inducing a *strain* within the metal (also see Table II). Part of the strain may be released through plastic deformation and/or formation of pores within the (solid) metal. However, the elasticity

TABLE II The average coefficients of thermal linear expansion (CTE) for nickel and polycrystalline alumina. The data actually used in the assessment within the text are marked by (*)

	Measured data [21, 24]			Interpolated or extrapolated data		
	Temperature range [°C]			Temperature range [°C]		
Material	From	to	CTE [10^{-6}·m·°C^{-1}]	From	to	CTE [10^{-6}·m·°C^{-1}]
Nickel	20	100	13.30	20	1000	16.45
		200	13.90	20	1400	17.11
		300	14.40	1000	1400	(*) 18.74
		400	14.80			
		500	15.20			
		900	16.30			
Alumina	0	20	4.60	1000	1400	(*) 9.50
		500	7.10			
		1000	8.10			
		1200	8.30			
		1400	8.50			

Note. For interpolation: if $l_1 - l_0 = \alpha_{01}\cdot(T_1 - T_0)$ and $l_2 - l_0 = \alpha_{02}\cdot(T_2 - T_0)$, then $l_2 - l_1 = \alpha_{12}\,(T_2 - T_1) = \alpha_{02}\,(T_2 - T_0) - \alpha_{01}\cdot(T_1 - T_0)$, where l_j [m] is the length of the system at temperature T_j [°C], α_{ij} [10^{-6} m °C^{-1}] is the CTE of the system for the temperature range from T_i to T_j. For extrapolation a logarithmic trend is assumed for α_{0j}. The coefficient of thermal volume expansion is 3α, and thus $\Delta V/V_0 = 3(\alpha_{\text{nickel}} - \alpha_{\text{alumina}})\cdot \Delta T$ for Ni bonded to alumina, and $\Delta V/V_0 = 3\alpha_{\text{nickel}}\cdot \Delta T$ for unconstrained Ni.

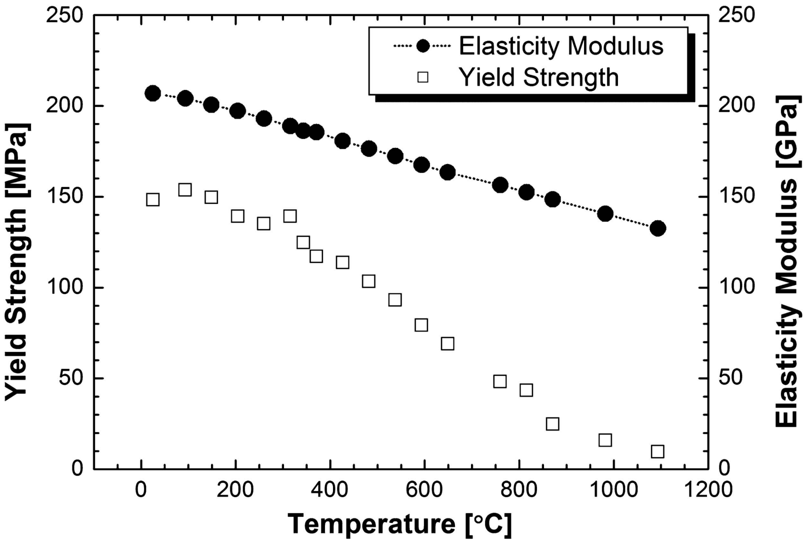

Figure 2 The yield strength and Young's modulus of elasticity of Ni, as a function of temperature, according to reference [23].

of the metal increases with decreasing temperature (see Fig. 2), and an elastic strain may produce *stresses* within the metal, especially in the interfacial region. Eventually, when these stresses become sufficiently high, they may overcome the bonding strength of the metal-ceramic join, and cause flawing and disjoining at the interface. This is consistent with the experimental results indicating that the interfacial voids form only when the drop dimension is above a critical value, as the stresses within the metal increase with the drop dimension. Finally, since alloying with Al or S prevented formation of interfacial voids, it is concluded that alloying with these elements enhances the mechanical strength of the Ni-sapphire join (in contrast with what was previously believed for S at Ni-Al_2O_3 interfaces [25, 26]). Similarly, it appears that the join made by Ni with an **A** surface of sapphire is stronger than that made with a **C** surface.

5. Summary and conclusions

Sessile drop wetting experiments of liquid Ni, Ni(2at.%Al) and Ni(0.003at.%S) on the basal surface of sapphire were conducted under extremely controlled working conditions, at 1500°C. Inspection of large pure Ni sessile drops from the wetting experiments revealed the presence of voids at the interface made with the basal surface of sapphire substrates. To the authors' best knowledge, this is the first report on the formation of voids at the interface of a metal sessile drop with a ceramic substrate. The results from this work indicate that voids form at the

Ni-sapphire interface only above a critical dimension of the sessile drop, to relieve residual thermal stresses in the metal drop. Alloying with Al or S hinders formation of voids at the interface by reducing the metal-sapphire interface energy. Thus formation of interfacial voids depends on the volume of the drop, which affects the total strain energy; and on the composition of the drop, which affects interfacial wetting and adhesion.

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References

1. A. E. MURUT and C. L. WHITE, *Acta Mater.* **45** (1997) 2547.
2. W. HU, P. KARDUCK and G. GOTTSTEIN, *ibid.* **45** (1997) 4535.
3. J. G. SMEGGIL, E. L. PARADIS, A. J. SHUSKUS and N. S. BORNSTEIN, *J. Vac. Sci. Techn. A* **3** (1985) 2569.
4. B. A. PINT and L. W. HOBBS, *Oxidation of Metals* **41** (1994) 203.
5. W. HU, W. WUNDERLICH and G. GOTTSTEIN, *Acta Mater.* **44** (1996) 2383.
6. X. SUN and J. A. YEOMANS, *J. Mater. Sci. Techn.* **12** (1996) 29.
7. G. VEKINIS, E. SOFIANOPOULOS and W. J. TOMLINSON, *Acta Mater.* **45** (1997) 4651.
8. B. J. DALGLEISH, E. SAIZ, A. P. TOMSIA, R. M. CANNON and R. O. RITCHIE, *Scripta Metall. Mater.* **31** (1994) 1109.
9. D. M. LIPKIN, J. N. ISRAELACHVILI and D. R. CLARKE, *Phil. Mag. A* **76** (1997) 715.
10. D. M. LIPKIN, D. R. CLARKE and A. G. EVANS, *Acta Mater.* **46** (1998) 4835.
11. R. BRYDSON, H. MÜLLEJANS, J. BRULEY, P. A. TRUSTY, X. SUN, J. A. YEOMANS and M. RÜHLE, *J. Microscopy* **177** (1995) 369.
12. J. T. KLOMP, *Mater. Res. Soc. Sym. Proc.* **40** (1985) 381.
13. G. LEVI, W. D. KAPLAN and D. R. CLARKE, *Inter. Sci.* **12** (2004) 73.
14. V. MERLIN and N. EUSTATHOPOULOS, *J. Mater. Sci.* **30** (1995) 3619.
15. G. LEVI and W. D. KAPLAN, *Acta Mater.* **51** (2003) 2793.
16. P. D. OWNBY and J. LIU, *J. Adh. Sci. Tech.* **2** (1988) 255.
17. J-H. CHOI, D-Y. KIM, B. J. HOCKEY, S. M. WIEDERHORN, C. A. HANDWERKER, J. E. BLENDELL, W. C. CARTER and A. R. ROOSEN, *J. Am. Ceram. Soc.* **80** (1997) 62.
18. W. W. ARMSTRONG, A. C. D. CHAKLADER and J. F. CLARK, *ibid.* **45** (1962) 115.
19. J. E. RITTER and M. S. BURTON, *Trans. Amer. Inst. Met. Eng.* **45** (1967) 115.
20. K. OGINO, K. NOGI and O. YAMASE, *Trans. ISIJ* **23** (1983) 234.
21. R. G. MUNRO, *J. Am. Ceram. Soc.* **80** (1997) 1919.
22. D. R. LIDE (ed.), "CRC Handbook of Chemistry and Physics", 84th ed. (CRC Press, LLC 2004) p. 12–220.
23. S. J. ROSENBERG, Nickel and Its Alloys (National Bureau of Standards Monograph 106, Washington DC 20234, 1968) p. 38, 39 and 63.
24. C. J. SMITHELLS, "Smithells Metals Reference Book", 7th edn, edited by E. A. Brandes and G. B. Brook (1992) chap. 14-4.
25. A. W. FUNKENBUSCH, J. G. SMEGGIL, N. S. BORNSTEIN, *Metal. Trans. A* **16** (1985) 1164.
26. W. J. QUADAKKERS, C. WASSERFUHR, A. S. KHANNA and H. NICKEL, *Mater. Sci. Techn.* **4** (1988) 1119.