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Reinitiation of substrate oxide undermining by Ni–P filler metals during wetting of nickel-base alloys

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The process of wetting of nickel and nickel–chromium substrates by nickel–phosphorus high-temperature brazing filler metals has been examined. The filler was found to wet the substrate by undermining the oxide layer on the substrate. Evidence was found that the undermining process is halted temporarily at discontinuities in the substrate oxide which typically occur above substrate grain boundaries. It is suggested that it is initially more favourable energetically for the filler to spread along the oxide defects than to continue undermining. Mechanisms for the reinitiation of undermining have been considered. It is proposed that undermining recommences after the onset of isothermal solidification of the filler spreading along oxide defects.

1. Introduction

Undermining of the substrate oxide layer has been observed by a number of workers [1–4] as a mechanism for the wetting of oxidized metallic substrates by liquid metals. These studies have concentrated either on initiation (in which the filler makes contact with the substrate metal–oxide interface) or on propagation (in which the filler spreads along the substrate metal–oxide interface) of undermining. However, in our previous work [5], a correlation was observed between the presence of discontinuities in the substrate oxide layer and the impeded spreading of nickel–phosphorus filler on nickel–chromium substrates. This correlation lead to the suggestion that undermining must be reinitiated after the filler makes contact with a discontinuity in the substrate oxide and that the reinitiation process controls the final extent of spreading. The current paper examines both the evidence for, and the possible mechanisms of, a reinitiation process.

2. Experimental procedure

Examination of the substrate oxide undermining process was conducted using discs (0.6 mm nominal diameter and 51 μm thick) of an Ni–11 wt % P–0.1 wt % C filler (A.W.S. designation: BNi-6) preplaced on a range of nickel and nickel–chromium substrates (Ni–0, 5, 10, 15 and 20 wt % Cr). Dynamic observations of the spreading process were made using hot-stage light microscopy together with video recording. These allowed the average diameter of the droplet and the displacement of individual solid–liquid interfaces to be measured subsequently as a function of holding time. A brazing temperature of 980 °C and a vacuum of 10^{-5} mbar were employed for these experiments.

Of the two types of measurement made, average droplet diameters were employed when comparison of different conditions was required, as they demonstrated a reasonable degree of repeatability (see Section 3.2). In comparison, interface displacement measurements provided more detailed information on individual propagation and reinitiation stages.

The hot-stage light microscopy results were correlated with those of sessile drop tests conducted at 980 °C at vacua of between 5×10^{-6} and 7×10^{-5} mbar. These pressures were achieved by evacuating the system to below 5×10^{-6} mbar and then readmitting sufficient air to attain the desired working pressure.

The results of the hot-stage spreading tests were correlated with scanning electron microscopy (SEM) observations of the oxide layer and laser microprobe mass spectrometry (LAMMS) and energy dispersive X-ray (EDS) analyses.

3. Results and discussion

In order to establish the role of a reinitiation process in spreading, four aspects must be examined:

(i) evidence for the occurrence of the reinitiation process;

(ii) correlation of the reinitiation process with discontinuities in the substrate oxide layer;

(iii) evidence for the control of undermining by reinitiation;

(iv) mechanisms giving rise to the reinitiation process.

Each of these areas will now be considered.

3.1. Occurrence of reinitiation and correlation with discontinuities in the substrate oxide

If a reinitiation process occurs during spreading, it would be expected that the propagation of the filler over the substrate surface would occur in a stepwise

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rather than a uniform manner. In Fig. 1, it is clear that the filler propagates in an irregular stepwise manner in which a series of rapid spreading stages (labelled S) are interspersed with holding periods (labelled H). Thus, the occurrence of a reinitiation process is supported.

During the holding periods, the main liquid–solid interface remains stationary, although strands of filler flow ahead of the main spreading front. These strands do not produce a significant advance of the liquid–solid interface and therefore do not appear in the measurements. Nonetheless, they are important in the mechanism of reinitiation (as is discussed in Section 3.3).

When the spreading results described above were correlated with SEM, LAMMS and EDS observations, it was found that each of the holding stages corresponds to a discontinuity in the substrate oxide which exposed the filler to the furnace atmosphere (as shown in Fig. 2 for different types of discontinuity). The presence of the chromium-free and phosphorus-rich BNi-6 filler could be readily identified at defects in the oxide, because the composition differed markedly from the phosphorus-free and chromium-rich substrate oxides present on Ni–Cr substrates. Moreover, when preoxidized substrates were used, which produced prominent discontinuities, the process could be observed dynamically in the hot-stage light microscope. Two types of substrate oxide discontinuity were observed; firstly, intragranular pores and, secondly, shear type cracks above substrate grain boundaries (the shear type cracks appeared to be associated with the formation of pores in the substrate grain boundary below the oxide). However, only the substrate grain-boundary defects (oxide cracks) were found to impede spreading.

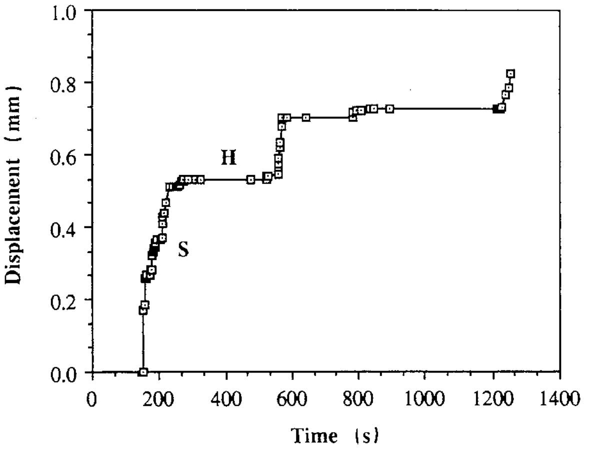

Figure 1 Stepwise propagation of BNi-6 over an Ni–10 wt % Cr substrate (S = spreading stage, H = holding stage).

From correlation of dynamic hot-stage light microscope and post-spreading SEM results, it was found that the thin strands of spreading that occur during the reinitiation stages corresponded to spreading along the base of the defects in the substrate oxide. Some tendency to produce similar strands of filler was observed at those grain boundaries for which oxide discontinuities were not produced (as indicated by lifting of the oxide layer above the boundary). However, these strands occurred to a lesser extent than was the case where an oxide discontinuity was present.

3.2. Evidence for the control of substrate oxide undermining by the reinitiation process

In the last section, evidence was presented for a process involving reinitiation of substrate oxide undermining. In order to examine the extent to which the reinitiation process controls spreading, hot-stage light microscope observations of spreading of BNi-6 on Ni–0, 5, 10, 15 and 20 wt % Cr substrates were employed. These results were correlated with SEM observations of the continuity of the substrate oxide layer on first reaching the brazing temperature and also after 20 min holding at temperature.

If reinitiation of substrate oxide undermining controls spreading, it would be expected that the occurrence of many discontinuities in the substrate oxide layer would correspond to a low final extent of spreading. However, complications can arise if the discontinuities in the substrate oxide either form or are removed (due to reoxidation) during holding at the brazing temperature. When the results of the hot-stage light microscopy experiments (Fig. 3) are compared

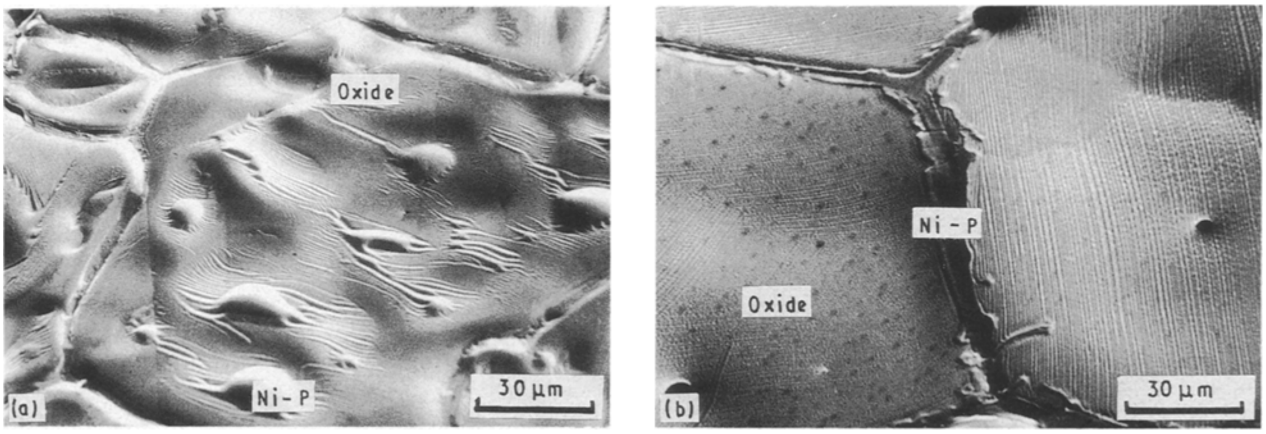

Figure 2 Escape of the BNi-6 filler from under the lifted substrate oxide, (a) at oxide pores, (b) at substrate grain boundaries (also note splattering of the filler over the adjacent oxide).

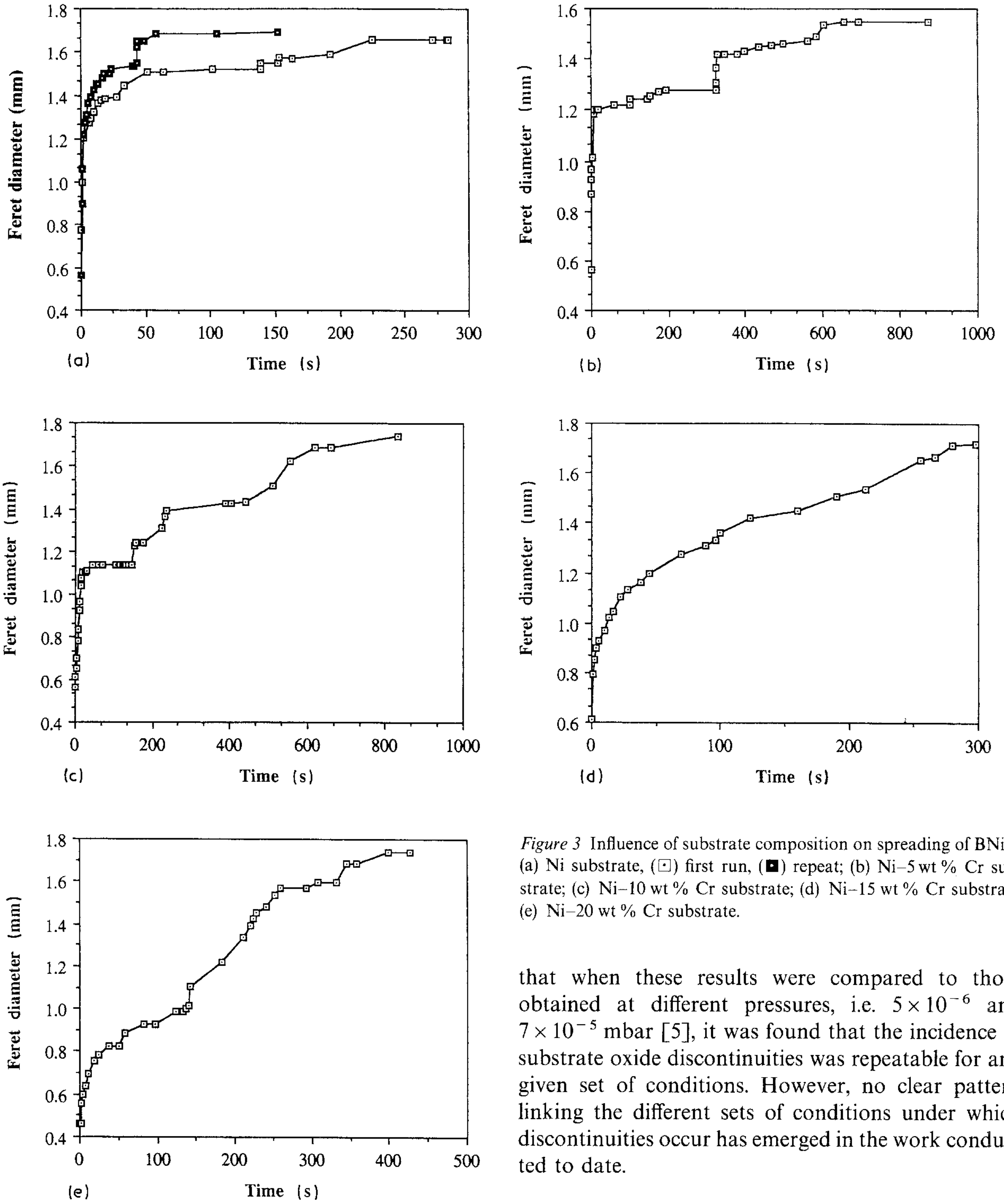

Figure 3 Influence of substrate composition on spreading of BNi-6. (a) Ni substrate, (□) first run, (■) repeat; (b) Ni–5 wt % Cr substrate; (c) Ni–10 wt % Cr substrate; (d) Ni–15 wt % Cr substrate; (e) Ni–20 wt % Cr substrate.

with the observations of the continuity of the substrate oxide, it can be seen that:

(i) high spreading rates correspond to either an initially continuous oxide even when this subsequently develops discontinuities (nickel substrate, Fig. 3a) or initially discontinuous oxides in which the discontinuities later reoxidize (15 or 20 wt % chromium substrates, Fig. 3d and e);

(ii) low spreading rates correspond to oxide layers that remain discontinuous throughout the duration of the tests (5 and 10 wt % chromium substrates, Fig. 3b and c).

These observations correlate well with control of spreading by the reinitiation process which depends upon the continuity of the substrate oxide layer. Note that when these results were compared to those obtained at different pressures, i.e. 5×10^{-6} and 7×10^{-5} mbar [5], it was found that the incidence of substrate oxide discontinuities was repeatable for any given set of conditions. However, no clear pattern linking the different sets of conditions under which discontinuities occur has emerged in the work conducted to date.

3.3. Mechanisms giving rise to the reinitiation process

During the reinitiation stage of spreading two phenomena have been observed:

(i) when the filler metal meets a discontinuity in the substrate oxide (and further undermining is impeded) it is exposed to the furnace atmosphere;

(ii) the filler continues to spread, to a limited extent, down the bare surface at substrate grain boundaries.

When these two phenomena are considered, it becomes clear that a need to reinitiate substrate oxide undermining could arise either because the mechanism allowing further undermining has been removed due to contact with the furnace atmosphere or because there exists a competition between, firstly, spreading along the oxide-free surface at those grain

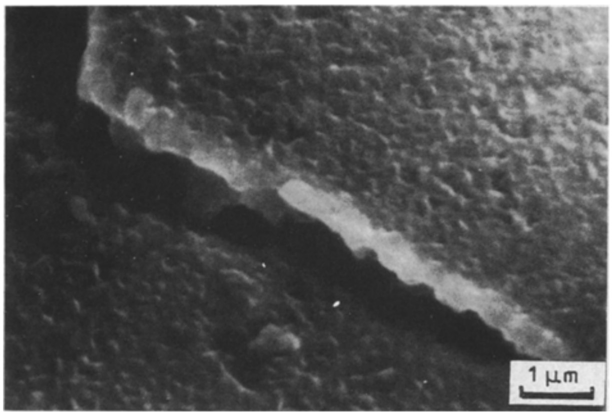

Figure 4 Lifting of the substrate oxide at oxide cracks (nickel substrate).

boundaries with oxide cracks and, secondly, under the bulk oxide. Each of these processes is considered below. In addition, a third process must be examined. During undermining, the oxide layer must be levered upwards so that the filler can spread underneath. Thus, at first sight, the loss of leverage when the filler escapes from under the oxide at discontinuities might seem important. In practice, however, in the shear type cracks shown in Fig. 4, the oxide is already levered upwards in the vicinity of the crack and hence loss of leverage would not seem to be of importance. Therefore, the applicability of the other two mechanisms (gas evolution and competitive spreading) is considered below.

If substrate oxide undermining is to occur, then the filler must be able to produce decohesion of the substrate metal and oxide, either at or ahead of the spreading filler front. Consider a case in which decohesion is aided by the pressure exerted due to a gaseous product of reaction between the filler and the substrate oxide. In this case, so long as the filler remains under the substrate oxide, then the gaseous product would remain trapped and could aid in decohesion. However, in the event of a gap in the substrate oxide, the gaseous product could escape to the furnace atmosphere and so further substrate oxide undermining would be impeded. This could, in turn, lead to a reinitiation period during which further reaction with the substrate oxide on the far side of the defect would be required in order to develop a new reservoir of the gaseous species. In contrast, spreading along the free surface associated with a defect in the substrate oxide defect would not be impeded and would therefore continue.

Whilst the events in the hypothesis described above are consistent with the experimental spreading observations, further consideration of the evidence for a gas pressure driven process is required. Thermodynamic calculations by Nakae [6] suggest that the activity of phosphorus in the BNi-6 filler is insufficient to allow significant reaction between phosphorus and the substrate oxide. However, the BNi-6 filler also contains significant quantities of carbon (0.1 wt %) and therefore a reaction between this carbon and the substrate oxide seems more likely. Similar reactions, liberating carbon monoxide, have been observed between substrate constituents and the substrate oxide by Lugscheider and Zhuang [7].

Experimentally, gas evolution was observed during spreading (with preoxidized substrates extensive gas bubble formation was frequently found to occur during spreading) and this also seems to have led to splattering of the filler over the substrate oxide around oxide discontinuities (Fig. 2b). In comparison, similar phenomena were not observed when using fillers such as Cu and Ni–Pd–Si. Unfortunately, it has not, at this time, proved possible to link these gas bubbles directly with carbon monoxide evolution as a result of reaction with the substrate oxide. Nonetheless, a comparison can be made between the spreading behaviour of the Ni–P filler and that of other fillers which do not have possible gas-evolving reactions. In previous work [5], it has been observed that Ni–Pd–Si and Cu fillers both show reinitiation stages in the spreading process. However, neither of these fillers would be expected to generate gaseous products as a result of reaction with the substrate oxide layer. Thus, the occurrence of gas evolution due to reaction with the substrate oxide does not provide a universal explanation of the reinitiation process, although such reactions may have some role in the spreading of BNi-6.

Consider, instead, a process involving competition between spreading along the base of oxide discontinuities at substrate grain boundaries and undermining of the bulk oxide layer. In hot-stage light microscopy investigations, a sequence of events relevant to such a competition was observed and these are now described. On first reaching a substrate grain boundary, the filler initially spreads down the boundary both in the case of substrate grain boundaries covered by continuous oxide layers and those with oxide cracks. These observations suggest that, in both cases, initially it is more favourable for the filler to spread down the substrate grain boundary than under the oxide covering the next substrate grain. However, whereas the grain-boundary spreading stage is protracted (lasting up to around 100 s) in the case of oxide layers with discontinuities at substrate grain boundaries, undermining of the bulk oxide on continuously oxidized substrates resumes almost immediately (usually within 1–2 s).

Termination of grain-boundary spreading would appear to be brought about by compositional changes in the filler due to interdiffusion with the substrate (Table I). Whereas the composition of the main filler droplet remains relatively constant (due to its relatively small surface area to volume ratio), the thin bands of filler over the substrate grain boundaries rapidly become depleted in the melting-point depressant phosphorus. The effect of these compositional changes is not sufficient to produce complete isothermal solidification of the grain-boundary spreading regions. Instead grain-boundary spreading becomes sluggish and is eventually replaced by undermining of the oxide on the adjacent substrate grain.

Whilst the occurrence of compositional changes in the filler accounts for the termination of the grain-boundary spreading process, it does not, directly, explain the difference in the extent of grain-boundary

TABLE I Filler compositions for main and substrate grain-boundary spreading fronts

Initial substrate Cr content (wt%)	Filler composition (mean and S.D.[a]) (wt. %)			
	G.B. spread[b]		Bulk spread[c]	
	Cr	P	Cr	P
0	0.1 (0.0)	1.7 (0.5)	0.0 (0.0)	11.0 (0.5)
5	4.0 (1.0)	1.1 (0.5)	1.2 (0.3)	11.1 (1.5)
10	10.7 (2.6)	0.7 (0.2)	3.3 (0.4)	11.7 (0.3)
15	14.5 (3.2)	1.0 (0.2)	4.3 (0.2)	11.3 (0.3)
20	24.4 (7.8)	0.6 (0.1)	9.7 (3.1)	8.4 (4.0)

[a] Main figures give mean values of at least seven analyses, bracketed figures give standard deviations (S.D.).

[b] Composition of regions of filler metal that have spread along substrate grain boundaries.

[c] Composition of the main filler front after spreading.

spreading between cracked and uncracked oxide layers. An additional explanation for this difference is now considered. In the case of continuous oxides, the rate of filler displacement down the boundary (at the commencement of the grain-boundary spreading stage) was similar to that under the bulk oxide during the last transgranular spreading step. However, in the case of discontinuous oxides, the initial rate of spreading down the boundary was approximately twice that under the bulk oxide on the preceding substrate grain. With both continuous and discontinuous oxides, spreading along substrate grain boundaries was decelerated by interdiffusion with the substrate and this process appeared to occur at a roughly similar rate in both the continuous and non-continuous oxide cases. However, given the greater initial velocity of spreading along the grain boundaries with oxide discontinuities, a longer period elapsed before spreading along the boundaries became sufficiently sluggish for grain-boundary spreading to be replaced by undermining. Hence, longer reinitiation stages are observed for substrate grain boundaries with oxide discontinuities than for those with continuous oxides.

Clearly the most important factor in the process outlined above is the greater rate of spreading along grain boundaries with oxide cracks than along oxide covered grain boundaries. The most obvious explanation of this difference in spreading rate on the bare metal present at the base of the cracks and by undermining of the bulk oxide is that the necessity of lifting the oxide layer impedes spreading. Comparison of spreading on otherwise similar substrates with thick and thin oxide layers confirms that increasing the difficulty of lifting the oxide, by increasing its thickness, impedes spreading. In the Appendix, a hypothetical model for the influence of this effect on the kinetics of the spreading process is presented using data for the system Ni(s)/Ni(l)/Al_2O_3(s).

In summary, of the mechanisms considered for the reinitiation of substrate oxide undermining (i.e. leverage, gas evolution and competition between grain-boundary and transgranular spreading), only the competitive spreading process is compatible with the observed spreading behaviour.

4. Conclusion

An investigation has been made of the process of reinitiation of substrate oxide undermining with a Ni–P filler on Ni–Cr substrates. As a result of this investigation the following conclusions have been reached.

1. Reinitiation has been correlated with the presence of discontinuities in the substrate oxide layer at substrate grain boundaries.
2. A reinitiation mechanism dependent upon leverage of the oxide is not compatible with the shear type defects observed in the substrate oxide layers.
3. The escape of gaseous products formed by reaction between filler constituents and the substrate oxide may, in part, account for the reinitiation process when using some fillers. However, the mechanism is not universally applicable.
4. Reinitiation correlates with a competition between spreading along substrate grain boundaries at oxide cracks and undermining of the bulk substrate oxide.
5. The grain-boundary spreading process is initially more favourable than undermining of the bulk oxide. However, it is terminated by compositional changes in the filler.

Appendix. Model of reinitiation of substrate oxide undermining

The change in interfacial energy produced by undermining of a unit area of an adherent oxide layer, $\Delta\gamma_u$, is given by

$$\Delta\gamma_u = \gamma_{sl} + \gamma_{ol} - \gamma_{os} \quad (1)$$

where γ_{sl} is the solid substrate–liquid filler interfacial energy, γ_{ol} the solid substrate oxide–liquid filler interfacial energy; and γ_{os} the solid substrate oxide–solid substrate interfacial energy.

In comparison, at defects in the oxide at substrate grain boundaries, spreading may occur along the free surface at the base of the defect (liberating $\Delta\gamma_f$ per unit area spread over). and also into the grain boundary (liberating $\Delta\gamma_g$ per unit area spread over). The values of $\Delta\gamma_f$ and $\Delta\gamma_g$ may be obtained as follows

$$\Delta\gamma_f = \gamma_{sl} + \gamma_{lv} - \gamma_{sv} \quad (2)$$

$$\Delta\gamma_g = 2\gamma_{sl} - \gamma_b \quad (3)$$

where γ_{lv} is the liquid filler–vapour interfacial energy, and γ_b the substrate grain-boundary energy.

Using the Ni(s)/Ni(l)/Al_2O_3(s) system as the nearest available model for Ni or Ni–Cr(s)/Ni–P–C(l)/NiO or Cr_2O_3(s) systems, and data drawn from a number of sources [8–11], the values of $\Delta\gamma_u$, $\Delta\gamma_f$ and Δ_g may be obtained as -125, -289, and -372 mJ m^{-2}, respectively (including an allowance of 100 mJ m^{-2} for reduction in γ_{ol} due to interfacial reactions). These data may then be used to determine the rate of interfacial energy release produced by spreading along grain-boundary defects ($d\Gamma_b/dt$) and by undermining ($d\Gamma_u/dt$).

Consider a competition between unidirectional spreading along a grain-boundary defect of a fixed width w, and unidirectional spreading (with a front of width s) under the oxide on a substrate grain. The rate of interfacial energy release when spreading occurs along grain boundaries with oxide defects is given by

$$\frac{d\Gamma_b}{dt} = (w\Delta\gamma_f + z\Delta\gamma_g)\frac{dx_c}{dt} \quad (4)$$

where z is the depth of grain boundary penetrated by the filler (assumed constant), and dx_c/dt is the rate of spreading along the crack.

In comparison, the rate of interfacial energy release for unidirectional spreading under the oxide on a substrate grain boundary is given by

$$\frac{d\Gamma_u}{dt} = s\Delta\gamma_u\frac{dx_u}{dt} \quad (5)$$

where dx_u/dt is the rate of spreading under the substrate oxide. Experimentally, it is found that initially

$$\frac{dx_u}{dt} \approx \frac{1}{2}\frac{dx_c}{dt} \quad (6)$$

If this relationship is used in Equations 4 and 5, the minimum value, z_m, of z required to make $d\Gamma_b/dt$ greater than $d\Gamma_u/dt$, and hence make spreading along the crack (rather than undermining of the transgranular substrate oxide) energetically favourable, can be calculated as 903 nm (using an example of $s = 10$ µm and $w = 1$ µm which are compatible with experimental observations). Grain-boundary penetration depths in excess of 10 µm can be observed experimentally; thus (before the onset of isothermal solidification which impedes the grain-boundary spreading process) grain-boundary spreading will be preferred to undermining. Once solidification of the thin strand of filler on the grain-boundary commences, the rate of spreading along the boundary and depth of penetration into the boundary will decrease, which will favour a resumption of undermining of the transgranular substrate oxide.

If a similar analysis is performed for the case of a grain boundary without an oxide defect, for which $\Delta\gamma_f$ is replaced by $\Delta\gamma_u$ and for which the grain-boundary and transgranular spreading velocities are similar (as is observed experimentally) then z_m is found to be 3.02 µm. As with the case of an uncracked oxide, this small z_m value would be expected to result in grain-boundary, rather than transgranular, spreading. However, because this value of z_m is more than three times as large as that in the case of a cracked oxide, this system will be more rapidly affected by the onset of isothermal solidification (which will both decrease the rate of spreading along the boundary and the penetration depth into the boundary and hence encourage transgranular spreading). Thus, a more protracted grain-boundary spreading stage would be expected with an oxide layer containing grain boundary cracks than would be the case for an oxide layer without these features and this accords qualitatively with the experimental observations.

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