

Wettability and interface considerations in advanced heat-resistant Ni-base composites

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Abstract. Oxide fiber-reinforced Ni-base composites have long been considered as attractive heat-resistant materials. After several decades of active research, however, interest in these materials began to decline around mid-1990's due chiefly to 1) a lack of manufacturing technology to grow inexpensive single-crystal oxide fibers to be used in structural composites, and 2) fiber strength loss during processing due to chemical interactions with reactive solutes in the matrix. The cost disadvantage has been mitigated to a large extent by the development of innovative fiber fabrication processes such as the Internal Crystallization Method (ICM) that produces monocrystalline oxide fibers in a cost-effective manner. Fiber strength loss has been an equally restrictive issue but recent work has shown that it may be possible to design creep-resistant composites even when fiber surface reconstruction from chemical interactions has degraded the strength of extracted fibers tested outside the matrix. The key issue is the optimization of the composite- and interface structure. Reaction-formed defects may be healed by the matrix (or a suitable coating material) so that the fiber residing in the matrix may exhibit diminished sensitivity to flaws as compared to fibers extracted from the matrix and tested in isolation of the matrix. Generally, the Ni-base/Al₂O₃ composites exhibit acceptable levels of wettability and interface strength (further improved with the aid of reactive solutes), which are required for elevated-temperature creep-resistance. In order to harness the full potential of these composites, the quality of the interface as manifested in the fiber/matrix wettability, interface composition, interphase morphology, and interface strength must be designed. We identify key issues related to the measurement of contact angle, interface strength, and chemical and structural properties at the fiber/matrix interface in the Ni/alumina composites, and present the current state-of-the-art in understanding and designing the Ni/alumina interface. There should be no doubt that optimization of the interface- and composite microstructure through judicious control of the fabrication process and surface modification shall yield technologically promising Ni-base/oxide fiber composites.

Key words: Ni-base composites, wettability, interfaces, interfacial strength.

1. Introduction

The thermal efficiency of gas turbines and other devices transforming thermal energy to mechanical energy depends upon the upper temperature of a thermal cycle. Enhancement of inlet temperature has, therefore, always been a significant driving force to increase the operating temperature of heat-resistant alloys. Advances in materials have been accompanied by application of increasingly more elaborate thermal barrier coatings and cooling systems of turbine blades, the latter being a consumer of a rather high portion of the turbine power. Certainly, both a temperature drop across the coating thickness and achievable levels of cooling have their limits, so any improvement in the design of turbine blades will require materials capable of operating at higher temperatures.

Advances in the development of heat-resistant materials have included Ni-base superalloys containing heavy metals such as Re, W, Ta etc, which stabilize the γ' -phase in a γ -matrix, creep-resistant single crystal structures, *in-situ* composites produced by deformation processing and directional solidification of Ni- or Co-based eutectics and multi-component and off-eutectic composites based on intermetallics

Ni₃Al and NiAl, dispersion strengthened superalloys (e.g., TD-Nickel and HD-Nickel), in which the dispersed phase obstructs the dislocation motion and resists recrystallization and grain coarsening, and superalloys and intermetallics reinforced with refractory metal fibers (Mo, W, W-Rh, Nb) and ceramic fibers (primarily oxides, and to a lesser extent, SiC and Si₃N₄).

During the last two decades, Ni-Al intermetallics such as Ni₃Al and NiAl were actively considered as matrix materials for fiber-reinforced composites. Both Ni₃Al and NiAl possess relatively high melting points ($T_{m,NiAl} = 1950$ K, $T_{m,Ni_3Al} = 1638$ K), excellent oxidation resistance (improved even further by Zr or Hf alloying), high strength and relatively low density (e.g., 5860 kgm⁻³ for NiAl). These intermetallics also possess high modulus and high thermal conductivity. NiAl has been used as a coating material in aircraft engines, but in a polycrystalline form, the material is extremely brittle, and its strength above about 773 K is very low. For example, the room temperature yield strength (Y.S.) of NiAl is in the range of 120–300 MPa, but at 1300 K, the Y.S. is only about 50 MPa. The ductility of polycrystalline NiAl is nearly zero below about 500 K. The ductility of NiAl can be improved via dual-phase toughening and microalloying, and its high-temperature strength can

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be enhanced through fibrous reinforcement. As NiAl exists over a wide range of stoichiometries, it has been possible to alloy it with Ti, Nb, Ta, Mn, Cr, Co, Hf, W, Zr and B to improve its mechanical properties, such as resistance to compressive creep, with Nb and Ta being especially effective. Similarly, small additions of tungsten to NiAl refine the grain size and inhibit grain growth, resulting in improved crack resistance.

The oxide fiber-reinforced Ni-matrix composites, at the very beginning of the modern composites study [1] were thought of as a way to escape the limitations imposed by the instability of the microstructure of superalloys at temperatures above ~ 1350 K. The appearance of sapphire fibers grown by the EFG method [2] in the mid 1960's stimulated interest in heat-resistant composites based on such fibers and Ni-base matrices. After nearly three decades of intensive research, however, interest in these materials (particularly, in NiAl/ Al_2O_3 composites) began to wane in mid 1990's due chiefly to two reasons. The first and the main reason was the absence of single-crystal oxide fibers sufficiently cheap to be used in structural composites (polycrystalline oxide fibers can be used up to 1473 K for short time and up to 1373 K for long time, due to recrystallization and grain boundary creep [3]). At the present time, the cost disadvantage has been mitigated by the development of Internal Crystallization Method (ICM) of fiber growth [4–7] that produces monocrystalline oxide fibers in a cost-effective manner. The method, analogous to techniques to grow bulk oxide crystals, allows bundles of monocrystalline or eutectic fibers to actually crystallize in continuous channels of a matrix, usually, Mo.

The second reason for skepticism toward the future of Ni-base/ Al_2O_3 composites was premised on then-prevailing conventional- but conceptually unsound view (which nevertheless had its genesis in sound experiments) that rejected a composite material as unfit for further investigation and use if the fibers extracted from the composite matrix and mechanically tested in isolation (i.e., outside the matrix), exhibited substantial strength loss due to chemical interactions with the reactive solutes of the matrix [8–10]. Thus, the conclusion that oxide fibers (actually, just sapphire) are not suitable reinforcement for Ni-based matrices and oxide composites system has no future, gained currency around the mid-nineties. It is noteworthy, however, that the Al_2O_3 composites generally exhibited high interfacial shear strength (usually, achieved with the aid of reactive matrix alloying), and showed promise of elevated-temperature creep-resistance.

The gradual decline in interest in the Al_2O_3 composites after initial observations of strength loss in extracted fibers slowed the technological development of these materials. In the last two decades, modeling of the mechanical behaviour of such composites under creep conditions was also conducted [4,5,11–17]. This research showed that it was possible to design composite microstructure with high creep-resistance and high fracture toughness even when fiber surface reconstruction and morphological changes from chemical interactions had degraded the strength of the fibers extracted from the matrix and tested outside the matrix. Of central importance to the implementation of this somewhat unorthodox, even revolutionary,

idea was the need to optimize the composite microstructure. The fiber/matrix interactions yield, indeed, defects in the fiber surface. But these reaction-formed defects as well as any original surface defects in the virgin fiber can be filled or healed by the matrix material so that the fiber residing in the matrix can exhibit diminished sensitivity to surface defects as compared to isolated fibers extracted from the matrix. The situation is analyzed in details in references [12,18].

In order to develop oxide-based/nickel-based composites for heat resistant applications, three main points should be emphasized: interface phenomena, availability of suitable fibers, and optimization of composite microstructure. Interface phenomena in Ni-base/oxide systems have always been considered a key issue in developing composites. However, it was only in the last two decades that essential contributions to understanding the interface phenomena in Ni based oxide fiber systems were made. In this paper we focus on some interfacial aspects of liquid-phase processed Ni-base composites for heat-resistant applications in which critical properties like creep resistance strongly depend upon the wetting and bonding at the interface.

2. Fabrication

Liquid-phase fabrication techniques for Ni-base composites include pressure infiltration, internal crystallization, and directional solidification. Initial trials to make sapphire-superalloy composites using vacuum infiltration were generally unsuccessful, and use of external pressure was necessary to overcome the poor fiber/matrix wettability. Infiltration is aided by alloying additions that promote wetting, such as Ti and Y, both of which are effective. NiAl-, Ni_3Al -, and superalloy (Hastelloy and Inconel 718)-based matrices have been reinforced with a variety of alumina fibers (single crystal sapphire, polycrystalline fiber FP, and PRD-166) using pressure infiltration casting technology [19–22].

Controlled directional solidification (DS) of Ni-base matrices has been used for the in-situ growth of composites. DS has been done using either the Bridgman technique or a containerless floating-zone technique on Ni-base superalloys, and NiAl and Ni_3Al -based eutectic and off-eutectic alloys containing Cr, Mo, W, V, Ta, and Re [23–29]. The second phase crystallizes as in-situ grown refractory fiber for strengthening. Improvements in toughness and creep resistance are also achieved. The floating-zone technique produces high-purity Ni-based composites because mold/metal reactions are eliminated. The DS techniques have also been used to grow ceramic fiber-reinforced composites. For this purpose, fibers are first incorporated in an off-eutectic NiAl-Me matrix (Me = Cr or W) using either pressure casting or a powder-based technique. This feed material is then directionally solidified to create a dual-phase matrix containing ceramic fibers with excellent bond strength and toughening potential.

The internal crystallization method (ICM), developed at Russian Academy of Sciences [4–7], allows bundles of monocrystalline or eutectic fibers to actually crystallize in continuous channels of a matrix, usually, Mo. The process is sim-

ilar to the methods used to grow bulk oxide crystals, and has been used to grow sapphire, mullite, yttrium-aluminum garnet (YAG), and alumina-YAG eutectic fibers. These fibers have been incorporated in Ni-base intermetallics and superalloys using pressure casting, thus yielding considerable gains in creep resistance. The ICM approach saves the cost and labor of combining fibers and matrices from separate sources.

Ni-matrix composites fabricated using the liquid-phase techniques generally exhibit better bonding than solid-state diffusion-bonded composites. For example, hot-pressed 'powder-cloth' NiAl/sapphire composites (made from fiber mats and plasma sprayed matrix powders) exhibit purely frictional bonding [30]. Interface contamination from binder residues interferes with interface development in these composites (e.g., interfacial segregation of residual carbon from PMMA and Teflon binders used in the composite facilitates fracture initiation). In addition, fiber damage during hot-pressing remains a major technological concern.

Another factor that favors liquid-phase route for composite fabrication is the Work of Adhesion, W_{ad} , of solid/solid and liquid/solid interfaces ($W_{ad} = \sigma_{lv}(1 + \cos \theta)$, where σ_{lv} is the surface tension, and θ is the contact angle). Table 1 summarizes the literature data on W_{ad} for a variety of Ni based alumina joints created under different test conditions. The value of W_{ad} for solid Ni/Al₂O₃ interface is approximately 518–645 mJm⁻² (depending upon the test chamber atmosphere) [31,32], whereas the value of W_{ad} of liquid Ni/sapphire interface is significantly higher (~1100 mJm⁻²) [34–36], which suggests that stronger interfaces may be designed using the liquid-phase techniques. In addition, liquid-phase techniques such as directional solidification permit microstructure design through creation of dual-phase aligned microstructure, fiber surface modification via precipitation of eutectic on ceramic fibers, fiber engulfment within the grains of the primary phase (thus eliminating matrix grain boundaries coincident on the fibers, which serve as crack initiation sites during loading), and growth of single-crystal matrix. These unique microstructure designs improve the composite's engineering properties. For example, controlled directional solidification of fiber-reinforced NiAl/sapphire composites with large oriented NiAl grains leads to significantly higher fiber/matrix bond strength compared to fine-grained, polycrystalline NiAl reinforced with sapphire. This is because in a polycrystalline matrix, grain boundaries coincident on the fibers promote crack nucleation even at relatively low stress levels.

Table 1

Approximate values of work of adhesion in Ni-base/Al₂O₃ systems

System	W_{ad} , mJm ⁻²	Reference
NiAl/sapphire	~1701	[38]
Ni/Al ₂ O ₃	~700	[74]
Ni/Al ₂ O ₃	~200–700	[41]
CoNi40/Al ₂ O ₃	~2800–2900	[41]
Ni/sapphire	~1100	[34–36,75]
NiAl/Al ₂ O ₃	~1438	[33]
Ni/Al ₂ O ₃	~645	[32]
Ni/Al ₂ O ₃	~518	[31]

3. Fiber-matrix wettability

3.1. Sessile drop test. For liquid-phase fabrication, the wetting behaviour of liquid matrix on the fiber plays a key role in the development of the fiber/matrix interface. The degree of wetting, usually characterized by the contact angle, θ , is, therefore, an important technological parameter for enhancing the joint strength. Contact angle measurements in Ni/ceramic couples have been reported in the literature [33–49]. Figure 1 shows the experimental sessile-drop data on contact angles measured between various Ni-base alloys and oxides (Al₂O₃, ZrO₂), carbides (SiC, TiC, Cr₃C₂), borides (TiB₂, TiB₂Cr), and nitrides (TiN, AlN) as a function of test temperature, contact time and matrix alloying. These data encompass both reactive and non-reactive couples. Generally, large obtuse contact angles are observed in Ni/Al₂O₃ [40,44,46] (e.g., at 1773 K, the values of θ are 128°, 133° and 141° in vacuum, H₂ and He atmospheres, respectively [43]) for the pure Ni/Al₂O₃ couples.

During the wettability test, alumina partially dissolves in the Ni droplet, and oxygen and Al released by the dissolution process diffuse into the drop and alter its chemistry. This dissolution process, however, does not significantly lower the contact angle, and large, non-wetting ($\theta > 90^\circ$) contact angles are attained. Suitable alloying of Ni droplet lowers the contact angle. For example, alloying Ni with Cr improves the wettability in Ni/Al₂O₃. Small quantities of Cr are sufficient to achieve good wetting and bonding in Ni/Al₂O₃; for example, the contact angle is close to 90° on both sapphire and polycrystalline alumina at 10% Cr in Ni, and the angle is ~75° at 20% Cr [35]. The solid/solid Ni/Al₂O₃ interfacial energy (σ_{ss}) is estimated to be in the range 2.0–2.7 Jm⁻² (from works by Hondros and by Nicholas, cited in [41]), whereas the solid/liquid interfacial energy (σ_{sl}) is estimated to be ~2.44 Jm⁻² [41]. In contrast, the solid/liquid interfacial energy in Ni-Cr/alumina couples is in the range of 1.3–1.8 Jm⁻² for Cr contents in the range 0.001% to 10% [35]. The contact angle is related to the interfacial energies from the Young-Dupre equation: $\cos \theta = (\sigma_{sv} - \sigma_{ls}/\sigma_{lv})$, where σ_{sv} and σ_{lv} are the surface energy of the solid and surface tension of the liquid, respectively. This equation shows that a decrease in σ_{ls} by Cr alloying will decrease the contact angle, θ , a conclusion that is consistent with the experimental results. In the case of Ni containing Fe and Pd, there is no change in the wettability with Al₂O₃ [34]; however, Cr improves the wetting of alumina by NiFe alloys without significantly attacking the alumina, although in NiPd alloys the addition of Cr up to 15% has little effect.

The contact angle measurements of Ni-base intermetallics (NiAl, Ni₃Al) on Al₂O₃ ceramics are scarce [33,42] in spite of the fact that these intermetallics have been considered as potential matrices for oxide fiber-reinforced Ni-base composites. No information on the wetting properties of near-stoichiometric single-phase NiAl with alumina could be found in the literature, and this represents an important area of study. The only data available on Ni-Al/alumina system are for much smaller Al content (for Al mole fraction, $X_{Al} \leq 0.25$) [33] that indicate two opposing effects of Al additions to Ni, and a maximum at $X_{Al} = 0.25$ in the curve of work of adhesion versus X_{Al} .

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Fiber coatings are frequently employed in the manufacture of composites for better compatibility with the matrix. Frequently, however, differences in the wetting and bonding behaviours are noted when the same chemical element is used as an alloying addition to the matrix and as a surface coating on

the ceramic fiber. For example, Ti films on Al_2O_3 improve the wetting and bonding in Al/ Al_2O_3 couples whereas Ti alloying of Al droplet does not improve the wetting [50]. Recently, the effect of alumina surface modification using Cr films on the wettability and bonding in Ni/ Al_2O_3 couples was investigated

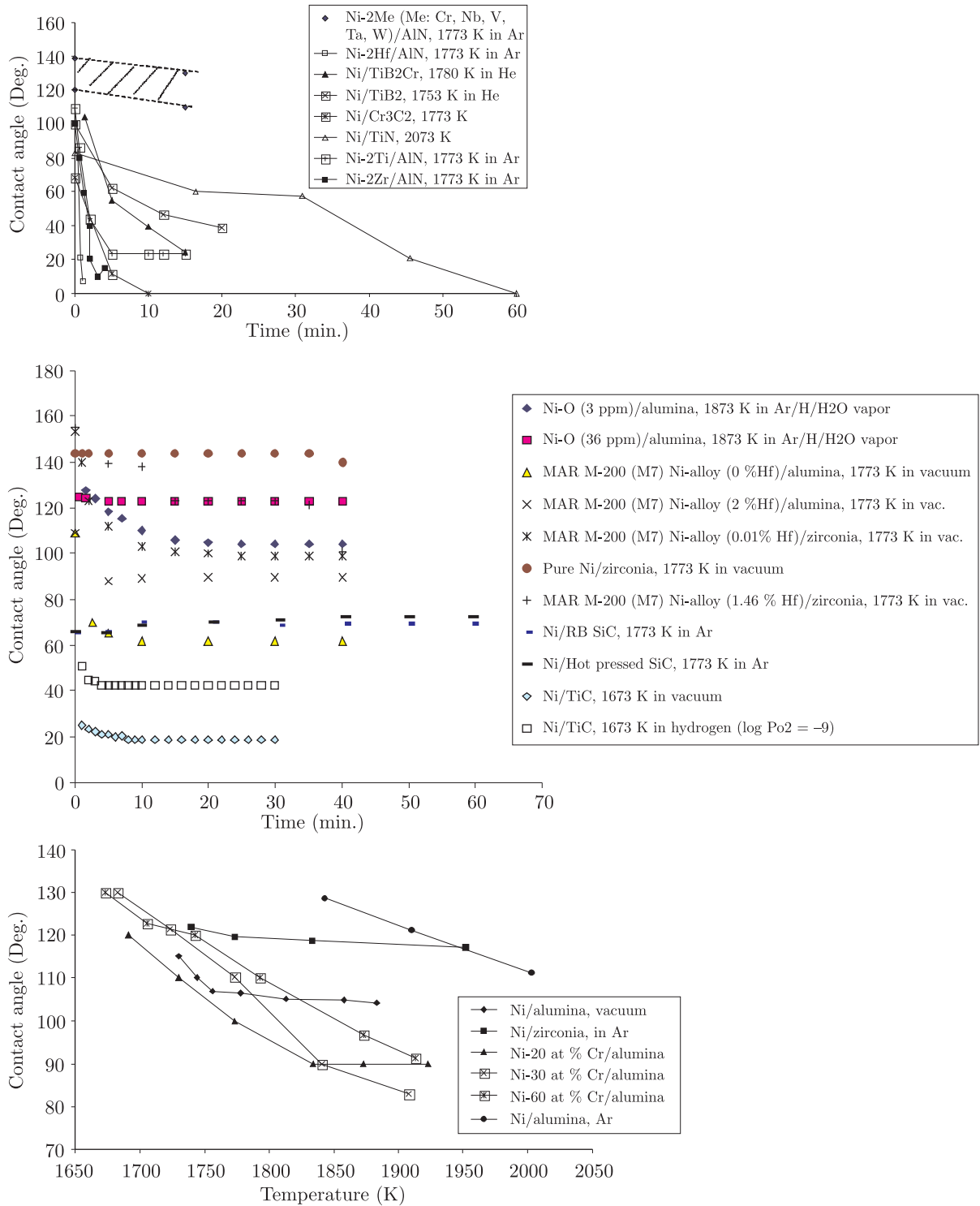


Fig. 1. Contact angle data of Ni-base alloys in contact with oxides (Al_2O_3 , ZrO_2), carbides (SiC, TiC, Cr_3C_2), borides (TiB_2 , TiB_2Cr), and nitrides (TiN, AlN). Data show the effect of temperature and time of contact

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[51]. The results show that Cr, either as an alloying addition to Ni or as a surface film on Al_2O_3 , improves the Ni/ Al_2O_3 wetting and bonding. Likewise, Cr alloying of NiAl improves the bond strength in NiAl/sapphire fiber composites. Thus, unlike Ti which is effective only as a coating rather than as an alloying element in the Al/ Al_2O_3 system, Cr is beneficial both as an interfacial coating and as an alloying addition in the

Ni/ Al_2O_3 system. Both polycrystalline and single crystal alumina substrates modified with vapor-deposited Cr films exhibit improved wetting with Ni [51]. For example, the contact angles decrease from 108° to 94° for $\text{Al}_2\text{O}_3^{\text{PC}}$ and from 100° to 98° for $\text{Al}_2\text{O}_3^{\text{SC}}$ (PC: polycrystalline, SC: single crystal) when Cr-coated Al_2O_3 is used in the wettability test.

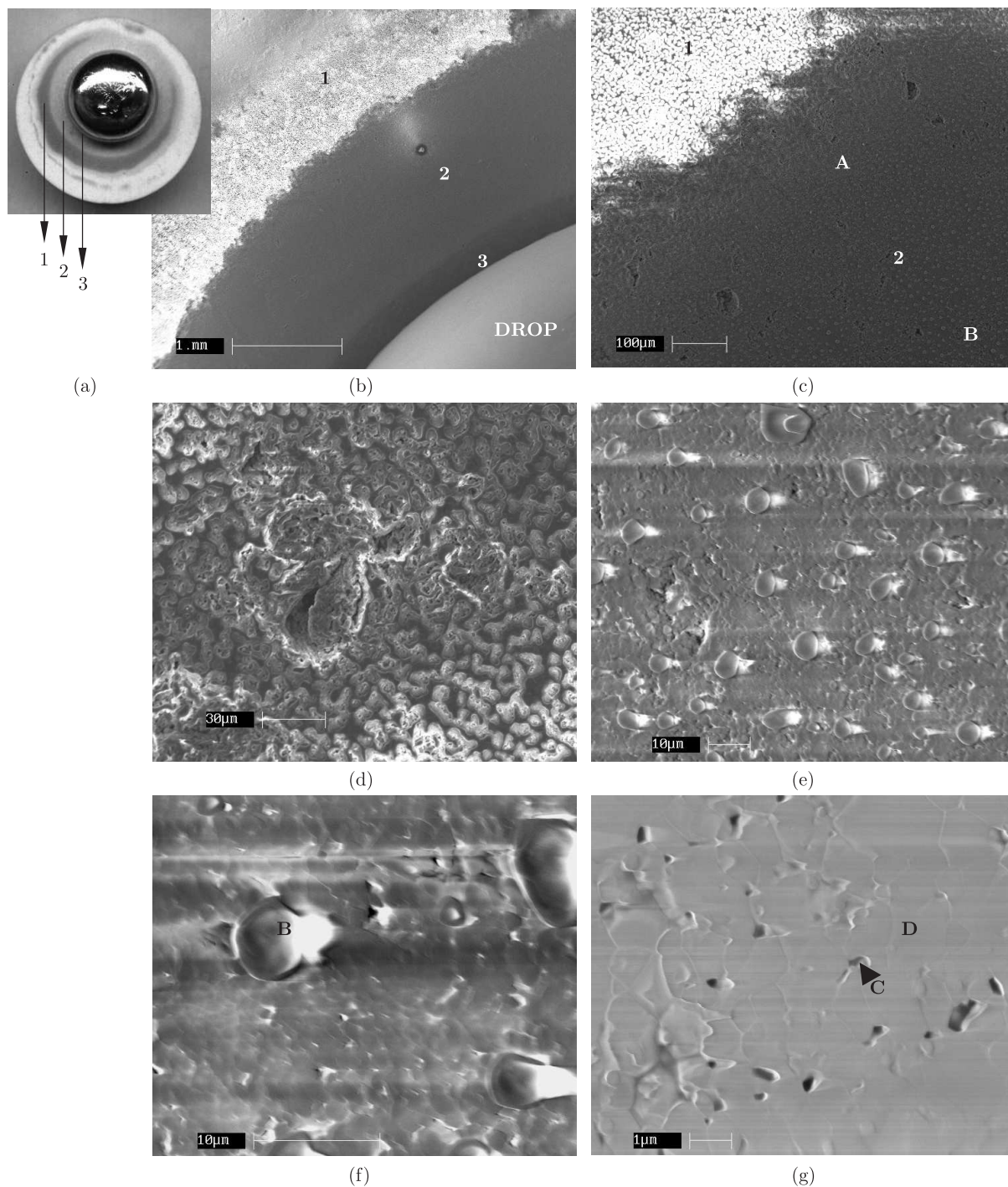


Fig. 2. SEM views of different regions in the Ni/Cr/ $\text{Al}_2\text{O}_3^{\text{PC}}$ (polycrystalline) sessile-drop sample at magnifications increasing from (a) to (g): (a) general view, (b) regions 1,2 & 3, (c) regions 1 & 2, (d) region 1, (e) & (f) region 2, and (g) region 3 (data after Ref. 51)

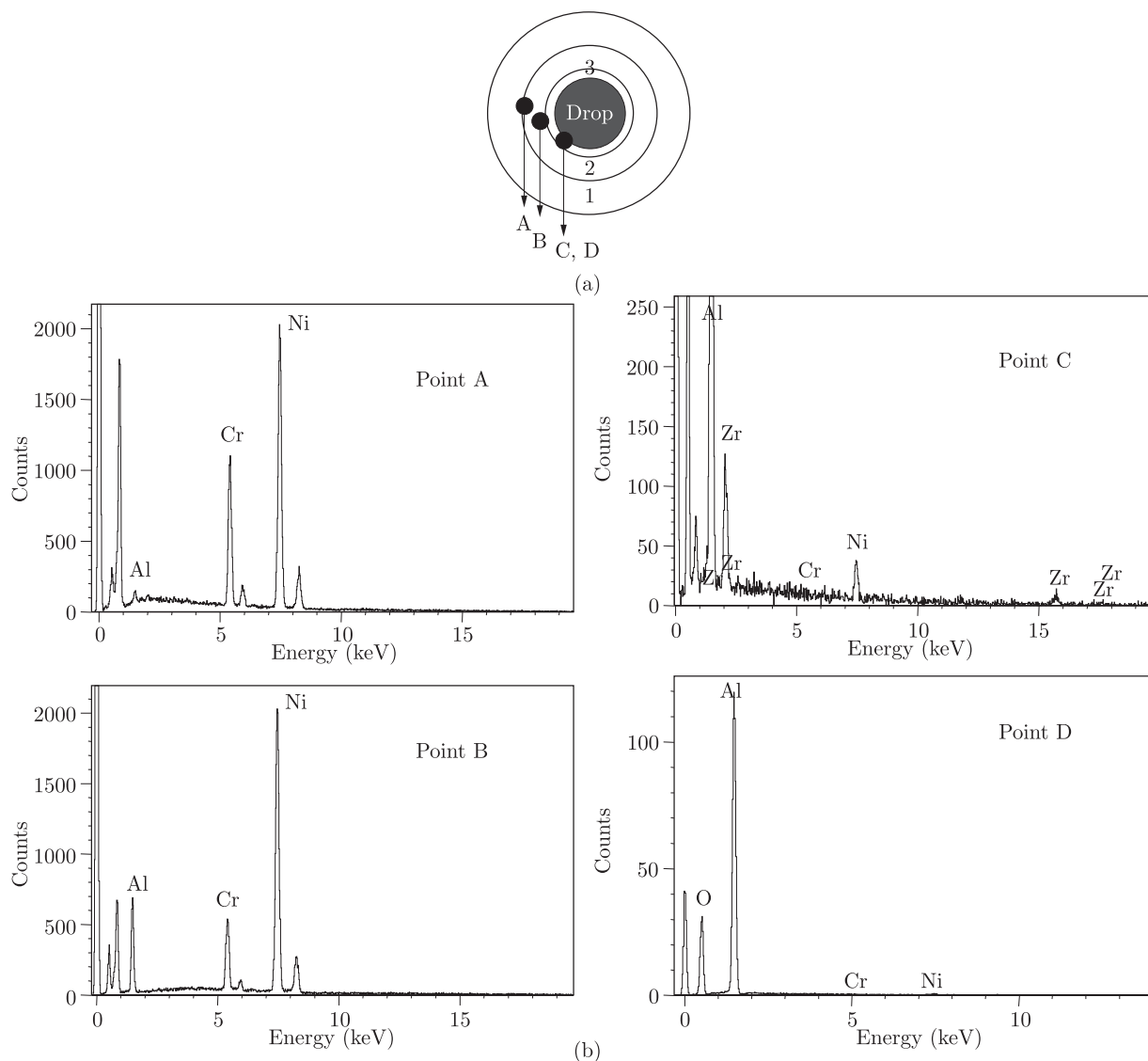


Fig. 3. The results of microanalysis of chemical composition made at Cr-coated $\text{Al}_2\text{O}_3^{\text{PC}}$ [51] surface near Ni-drop after the wettability test at 1773 K for 15 min; a) scheme of regions and point analysis; b) EDS spectra taken from points marked A, B, C and D in Fig. 2

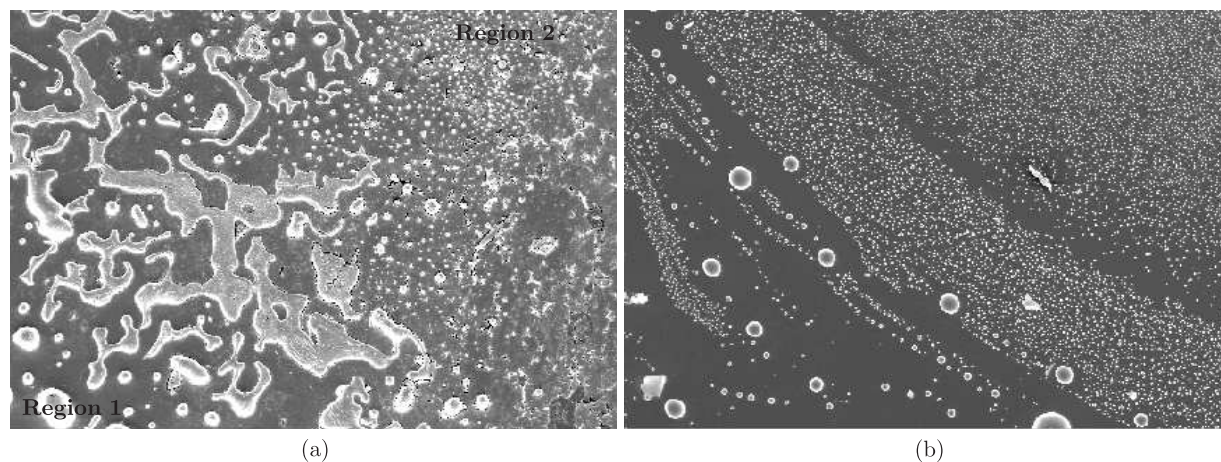


Fig. 4. SEM views of the surface of Ni/Cr/ $\text{Al}_2\text{O}_3^{\text{SC}}$ (single crystal) sessile-drop sample [51] recorded from the top of the drop showing (a) island-like structure of Cr-film in region 1, and (b) the droplets of different size in ring-like region 2 near the drop

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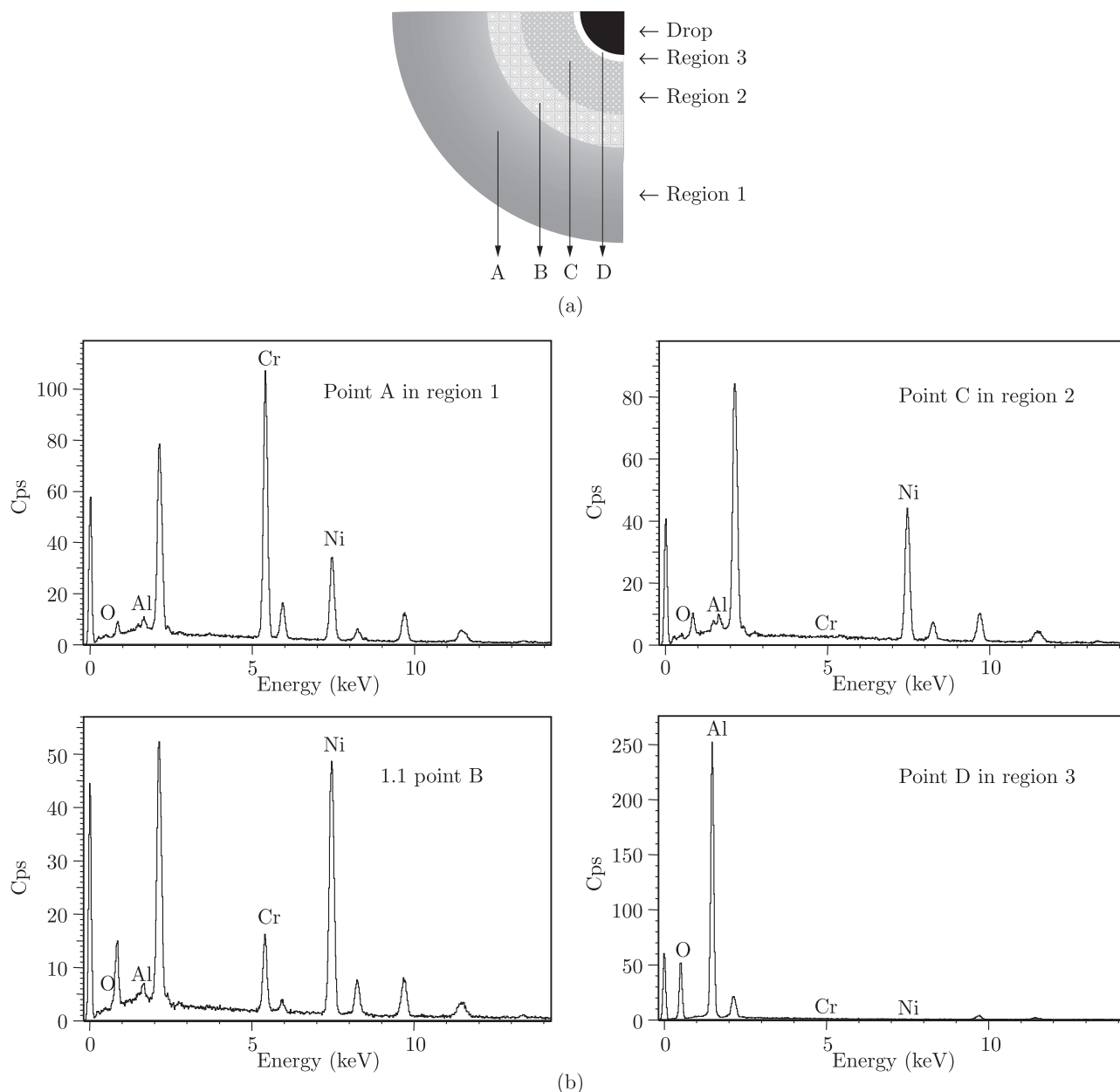


Fig. 5. The results of microanalysis of chemical composition at Cr-coated Al₂O₃^{SC} surface near Ni drop after the wettability test at 1773 K for 15 min [51]: a) scheme of regions and corresponding point analysis; b) EDS spectra taken from points A, B, C, and D

Figures 2 and 3 show the top views of solidified sessile drop samples in Ni/alumina and Ni/Cr/alumina, and the corresponding microanalysis. Significant changes in the morphology of Cr film surrounding the Ni droplet can be noted. In Ni/Cr/Al₂O₃^{PC}, three regions of dissimilar structure and composition form around the drop. The outer region 1 corresponds to the Cr-film, which is rough and discontinuous. Region 2 (~1.5–2 mm wide) has a different morphology, and is composed of a number of fine droplets; in the outer portion of this region (Point A), the droplets are very fine and Cr-rich while in the inner portion (Point B), the droplets are coarser and depleted in Cr. Region 3 (~0.2 mm wide), located just near the drop, is completely devoid of Cr, and contains very

minute quantities of Ni and Cr (Points C, D). Region 3, therefore, displays the surface structure of alumina substrate after a 30 min. direct contact with molten Ni, and represents an ‘opened’ interface due to solidification shrinkage and/or drop movement during the test. Frequently, inter-granular areas in Region 3 display small, Zr-rich voids (Point C) and Zr-free alumina grains (Point D) (a small quantity of ZrO₂ was added to alumina as a sintering aid).

With a single-crystal alumina substrate in the Ni/Cr/Al₂O₃^{SC} couple (Figs. 4 and 5), ring-like regions form around the Ni droplet; these regions are, however, less distinct than in Cr-coated polycrystalline alumina substrate. Moreover, compared to rough polycrystalline alumina, the Cr film on

smooth single-crystal alumina is unstable and discontinuous (a thin Au layer was deposited for SEM examination to prevent charging from the uncovered areas of alumina; the unmarked peaks in the spectra of Fig. 5 correspond to Au). On both types of alumina substrates, Ni is present even quite far from the liquid Ni droplet; this suggests an evaporation-deposition process which could be operative not only during isothermal hold at the wettability test temperature, but also during heating and cooling. To confirm this, a Ni/Cr/Al₂O₃^{PC} couple was heated under controlled atmosphere to 1680 K (i.e., below the melting point of Ni), and then suddenly cooled to room temperature. Even though Ni did not melt, a dark Ni-rich halo formed around the solid specimen of Ni, and the latter had bonded to alumina even under solid/solid contact in the absence of external pressure.

In the case of molten Ni in contact with Cr-coated Al₂O₃, the interaction between Ni and Cr-film, and between Ni and Al₂O₃ leads to interdiffusion and mass transfer. When Cr-coated alumina is used, evaporation and deposition of Ni forms a Ni-Cr film at the drop/substrate interface and around the Ni drop. An increase in O, Al and, particularly, Cr content in the Ni drop lowers the latter's melting point, leading to the formation of liquid Ni-Cr(Al,O) phase in the form of fine discrete droplets as shown in Figure 2e. Furthermore, due to a favorable CTE of Cr relative to Ni and Al₂O₃ (CTE_{Ni} = 13.3 × 10⁻⁶ K⁻¹, CTE_{Cr} = 6.2 × 10⁻⁶ K⁻¹, CTE_{sapphire} = 9.5 × 10⁻⁶ K⁻¹), better Ni/alumina bonding is achieved in Ni/Cr/Al₂O₃ couples as compared to uncoated couples.

Chromium films on alumina protect the latter from chemical attack by molten Ni. Surface asperities on bare (uncoated) Al₂O₃ substrates dissolve in molten Ni droplets during sessile-drop wettability test, leading to an "etched" or "polished" region concentric to the droplet. This dissolution process releases Al and O (which presumably form Ni-O clusters that are adsorbed on Al₂O₃), and if O is continuously removed from the reaction interface (as under a dynamic vacuum), then dissolution of the substrate can continue. A practical consequence of this is that alumina crucibles should be used for melting Ni in air but not under vacuum.

4. Adhesion

The adhesion strength of bi-material interfaces in ceramic/ceramic and ceramic/metal systems is generally characterized by bend test, fiber push-out test, and droplet push-off shear test. The bend test is widely used with ceramic/ceramic joints; however, with a metallic interlayer (as in brazed ceramics), data are strongly influenced by the braze layer thickness. Additionally, joining of ceramics is often done in the solid-state, and the measured bond strength is not comparable to the outcomes of the wettability test, or to the strength of the joints made via liquid phase joining techniques. In view of this, correlation of interfacial shear strength with the basic interfacial properties (θ and W_{ad}) is usually difficult. The need for relatively large samples and very specific requirements for sample preparation frequently make it difficult or even impossible to execute bend tests in ceramic/metal couples. The droplet

push-off shear test and the fiber push-out test permit a more direct measurement of the shear strength of joints, and of the fiber/matrix interface strength in composites, respectively.

4.1. Droplet push-off shear test. The droplet push-off shear test was developed to study the wetting-bonding relationship in metal/ceramic couples by measuring the contact angle of molten droplets on ceramics, and the shear stress required to debond solidified sessile droplets in contact with ceramic substrates at the conclusion of the wettability test. The test has been applied chiefly to Me/alumina couples (Me = Cu, Ag, Al, Ni, and Fe). In the Ni/Al₂O₃ system, a decrease in the bond strength of joints made via liquid/solid contact is observed with increasing contact angle (the bond strength is in the range of 71–111 MPa [39,52]). In contrast, the solid-state diffusion-bonded Ni/Al₂O₃ couples possess lower bond strength [41], typically, 16–60 MPa, when hot pressing is done in the temperature range of 1223–1323 K. As a rough generalization, therefore, liquid-phase techniques provide better interfacial bonding than solid-state fabrication techniques.

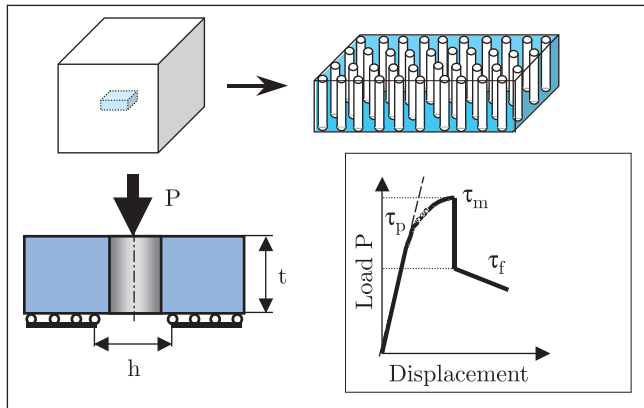
The conventional push-off shear test suffers from certain methodological limitations, mainly the difficulty of applying shear debond stress on thin (i.e., wettable) solidified droplets. An improved droplet push-off shear test (Fig. 6), developed at the Foundry Research Institute (Cracow) and described in detail in references [50,51,53–56], allows shearing of thin solidified sessile droplets in contact with ceramic substrates. The test is done by first carefully bisecting the solidified droplet/substrate couple perpendicularly to the substrate at the mid-plane of the contact circle, and then using one-half of the bisected couple for the push-off test (the other half is used for characterizing the interface structure and chemistry). The push-off test automatically records the load-displacement data up to failure under a constant strain rate. This technique has been applied to both non-reactive (Ni/alumina, Al/alumina and Al/AlN), and reactive (Al/Si₃N₄ and Al-Ti/Si₃N₄) systems at the Foundry Research Institute.

The improved droplet push-off shear test was recently used to directly measure the effect of Cr films on adhesion and its relationship to contact angle in Ni/Al₂O₃ couples [51]. Chromium additions to Ni have been known to lower the contact angle and increase the adhesion strength with alumina, but the effect of Cr as a surface film was not studied until recently. The improved droplet push-off shear test shows that Ni bonds to Al₂O₃^{PC} substrates better when Cr coatings are used (shear strength ~138 MPa) than in the absence of Cr coating (shear strength ~78 MPa). In the case of uncoated Al₂O₃^{SC}, shear strength measurements were difficult owing to a number of interfacial cracks that were visible through transparent alumina single crystals. These cracks weakened the Ni/Al₂O₃^{SC} joint, and precluded shear strength measurements. In contrast, in Cr-coated Ni/Al₂O₃^{SC} couples, the joints were free of cracks. This suggests that Cr interlayer serves as stress absorbing compliant layer.

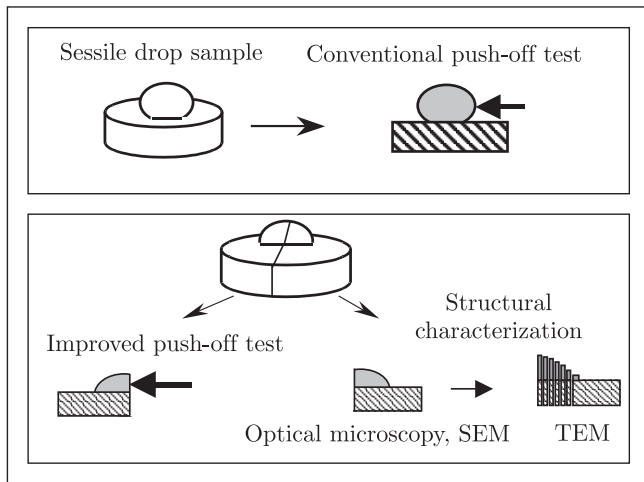
Chromium possesses good thermoelastic compatibility with both Ni and Al₂O₃, and Cr films indeed could serve as stress-absorbing compliant layers in Ni-base composites such

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as Ni/Al₂O₃ and NiAl/Al₂O₃. For example, the mismatch of the coefficients of thermal expansion (CTE) between Ni (or NiAl) and Al₂O₃ is rather large ($CTE_{Ni} = 13.3 \times 10^{-6} \text{ K}^{-1}$, $CTE_{sapphire} = 9.5 \times 10^{-6} \text{ K}^{-1}$ and $CTE_{NiAl} = 15 \times 10^{-6} \text{ K}^{-1}$). This results in thermal clamping stresses (compressive on the fiber and tensile in the matrix), which could cause matrix cracking in the vicinity of the fiber (the compressive stresses from radial clamping over the fiber length increase the fiber debond stress). Because chromium has a CTE intermediate between Ni (or NiAl) and alumina, an interlayer of Cr could serve as a stress-absorbing intermediate compliant layer ($CTE_{Cr} = 6.2 \times 10^{-6} \text{ K}^{-1}$).



Fiber push-out test



Droplet push-off shear test

Fig. 6. Schematic diagrams showing the improved droplet push-off shear test and the fiber push-out test methods to measure the interfacial shear strength

Figure 7 displays the contact angle and shear strength data in Ni/Al₂O₃ couples measured by various investigators. The results show that, as a general rule, high shear bond strength correlates with a low contact angle, consistent with the behaviour noted in other ceramic/metal systems such as Al/Al₂O₃ [57]. Some dispersion in the measurements arises from the different techniques (droplet push-off, bend-test etc.) employed by different investigators, and the different test conditions, and Ni alloy compositions used in contact angle mea-

surements. Figure 7 also shows the Ni/Al₂O₃ shear strength data in hot-pressed composite joints; these data are shown at an arbitrary value of the contact angle ($\sim 75^\circ$) because no direct measurements of contact angle could be obtained in hot-pressed couples. The scatter in the shear strength values of hot-pressed joints is due to variations in the chemical composition, structure, and processing of the alumina substrates. Figure 7 also shows that liquid-phase processed Ni/ceramic joints exhibit better bonding than solid-state joints. Extraneous factors such as interfacial defects and matrix plasticity could, however, mask this behaviour. It is, therefore, necessary to examine the experimental contact angle/shear strength correlations in light of the microstructure of the interface region.

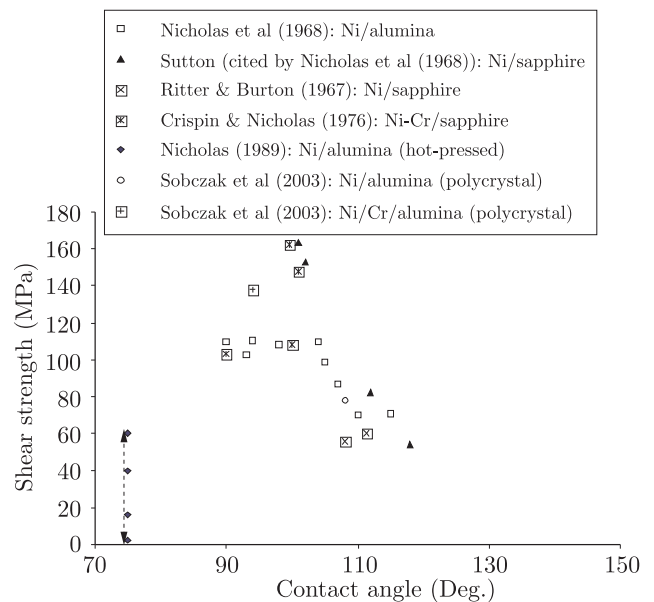


Fig. 7. Contact angle-shear strength relationship in some Ni/Al₂O₃ systems. Shear strength data on solid-state diffusion bonded Ni/Al₂O₃ composite joints are shown at an arbitrary value of the contact angle ($\sim 75^\circ$) because no direct measurements of contact angle were reported. The scatter in the shear strength values of hot-pressed joints is due to variations in the chemical composition, structure, and processing of the alumina substrates

4.2. Fiber push-out test. The fiber push-out test yields the interface strength of fiber-reinforced composites from the measurements of the compressive load on a single fiber that is required to debond and displace the fiber in the matrix. The test has been applied to a wide variety of ceramic-ceramic and metal-ceramic composites, such as SiC/Si₃N₄, Ti/SiC, TiAl/glass, Nb/sapphire, and NiAl/sapphire. In the conventional test, thin (100–1000 μm) composite wafers, ground and polished to reveal the fiber ends and the surrounding matrix structure, are mounted on a support block containing grooves that permit unobstructed sliding of individual fibers through the wafer with the help of a flat-bottomed microindenter attached to an INSTRON frame. The load-displacement data (and acoustic emission) are recorded, and apparent interface strength τ^* is obtained from the measured debond load, Q , and

the interfacial contact area, with $\tau^* = Q/(\pi Dt)$, where D is fiber diameter and t is the wafer thickness. Figure 8 shows typical load-displacement profiles from the fiber push-out test on actual NiAl/sapphire composites. These profiles mimic the schematic load – displacement profile of Fig. 6, which also displays the stresses corresponding to three load transitions that characterize the interfacial properties: τ_p (proportional shear stress, which signals the onset of inelastic deformation), τ_m (maximum shear stress at which the fiber debonds from the composite matrix), and τ_f (frictional shear stress for sliding of debonded fibers in the wafer); the maximum shear stress provides an estimate of the interface debond strength. Normally, the fiber push-out load-displacement data are examined in light of the fractographic observations of debonded interfaces to interpret the results on a semi-quantitative level.

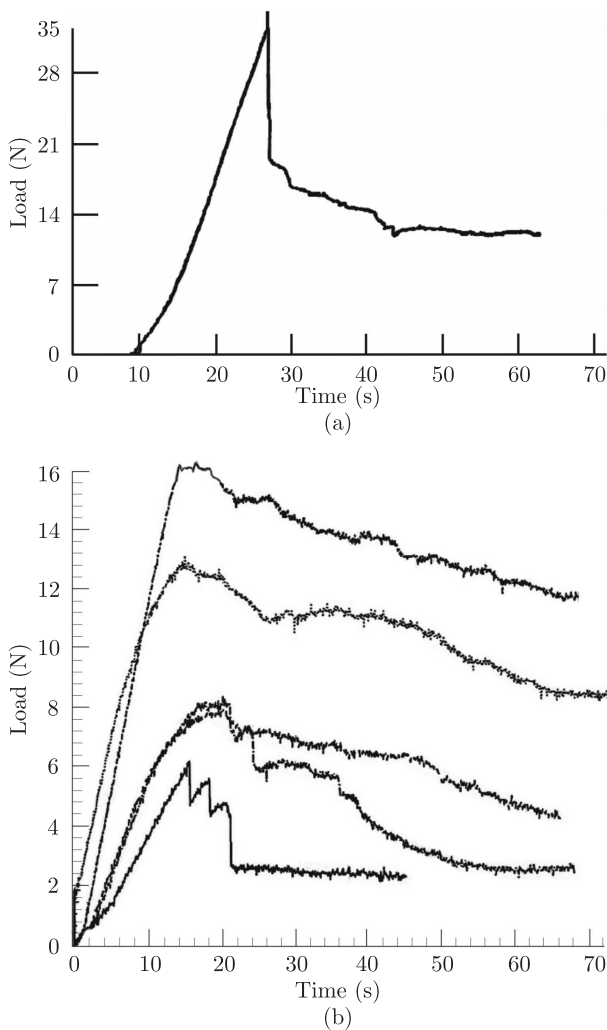


Fig. 8. Load versus time profiles from fiber push-out test on NiAl(Cr)/sapphire (top) and DS NiAl(Yb)/sapphire (bottom) composites. The different curves in the bottom figure correspond to separate fibers in discs of different thicknesses

Attempts have also been made to identify the stress at which cracks initiate at the fiber/matrix interface during fiber loading via interrupted push-out tests. For this purpose, the front- and the back-faces of each loaded fiber are viewed under a SEM after stopping the push-out test at different load

values [59,60]. The interrupted test is done on a large number of individual fibers in order to develop general conclusions concerning the crack initiation and propagation behaviours. Typical fractographic observations from the interrupted push-out tests on directionally solidified (DS) NiAl/sapphire composites (Fig. 9a) and hot-pressed, powder metallurgy (PM) NiAl/sapphire composites (Fig. 9b) are summarized in Figure 9 (PM composites are also referred to as PC or Powder-Cloth composites because they were fabricated using NASA's Patented PC process). These observations also take into account the effect of matrix structure in the vicinity of the fiber and the thickness of the wafer on the crack initiation behaviour. The test results are sensitive to the (t/h) ratio, where t is specimen thickness and h is the width of the hole in the support block over which the composite wafer is positioned prior to the fiber push-out test (Fig. 6 shows a schematic of the test configuration). In the DS composite wafers, the sapphire fibers were either anchored at grain boundaries (GB fibers) or engulfed within the grain interior (GI fibers) whereas in the PM composite wafers, the fibers were contacted by numerous grain boundaries. The results showed that in spite of the interfacial porosity (Fig. 9(a)) from the binder residue in the DS composites, the shear strength was significantly higher for the GI fibers than for the GB fibers and for the fibers in the PM composites. Based on these results, it was recommended that in order to realize the full potential of interfacial strengthening in the NiAl/sapphire composites, pressure cast feedstock (rather than binder-based PM feedstock) would be a better choice. Figure 9c summarizes the results of interrupted push-out tests on PM and DS composites: in thin ($t/h \leq 0.75$) wafers of PM (or PC) composites, front- and back-face interfacial cracks initiated as soon as the proportional shear stress, τ_p , was reached; however, no cracks formed at τ_p in thick wafers ($t/h > 0.75$), and the first evidence of cracking was noted in the vicinity of the maximum shear stress, τ_m . In the DS composites, there was no effect of the ratio (t/h) on the crack initiation behaviour (for $100 \mu\text{m} < t < 700 \mu\text{m}$); interfacial cracking occurred on both front and back faces of the composite wafers at τ_m for the GB fibers, whereas for the GI fibers in both thick and thin wafers, only backface cracks formed at τ_m . Such micromechanical and fractographic observations provide an empirical basis to understand the interface behaviour in fiber-reinforced composites.

Actually, a strict theoretical interpretation of results obtained in a fiber push-out test needs reasonable assumptions on nucleation and propagation of the interface crack under a rather complicated stress state. Perhaps, approaches based on ideas of fracture mechanics (e.g., [58]) are more promising than just straightforward calculation of the average shear stress, and accepting it as a measure of the interface strength. Attempts have also been made to account for matrix plasticity [61,62] during loading of fibers in a push-out test, but a complete understanding of all the features of the real behaviour is absent. Hence, the main use of the test outcomes is to study the relative effects of constituents' properties and fabrication parameters on the interface strength.

Virtually all well-known variants of the fiber push-out test apply to fibers of circular cross-section. Sometimes, however,

Wettability and interface considerations in advanced heat-resistant Ni-base composites

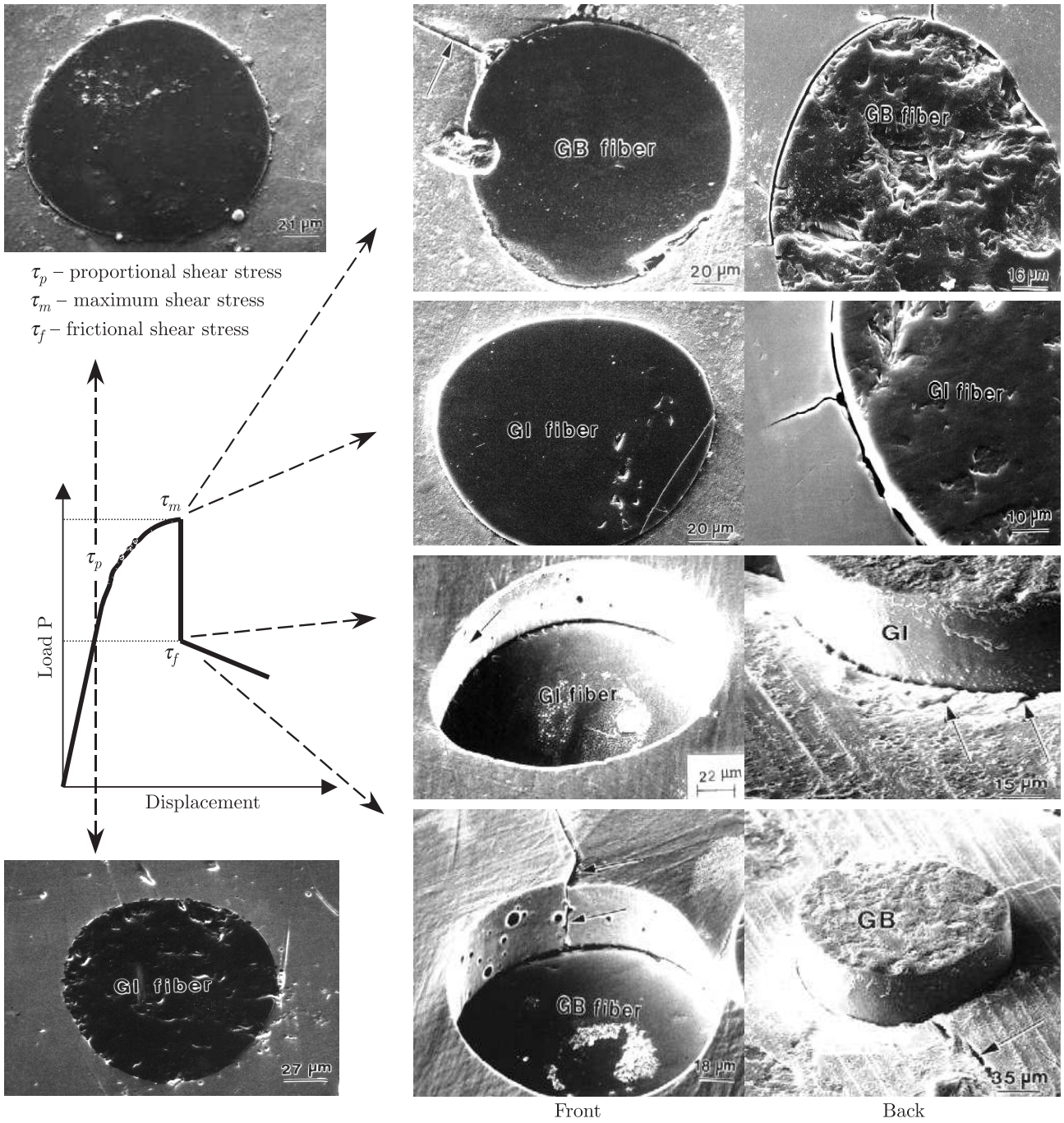


Fig. 9(a)

R. Asthana, S.T. Mileiko, and N. Sobczak

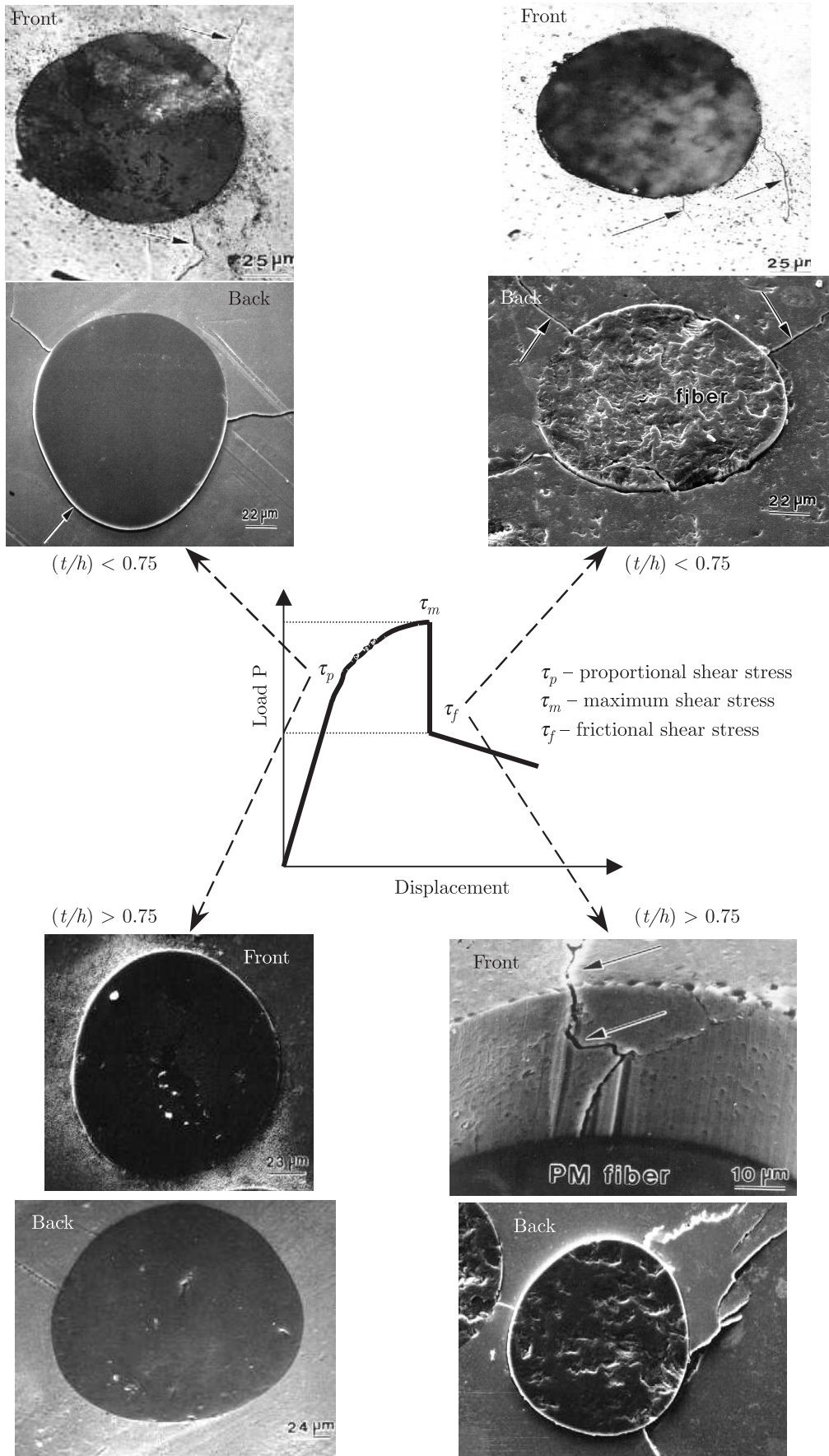


Fig. 9(b)

Wettability and interface considerations in advanced heat-resistant Ni-base composites

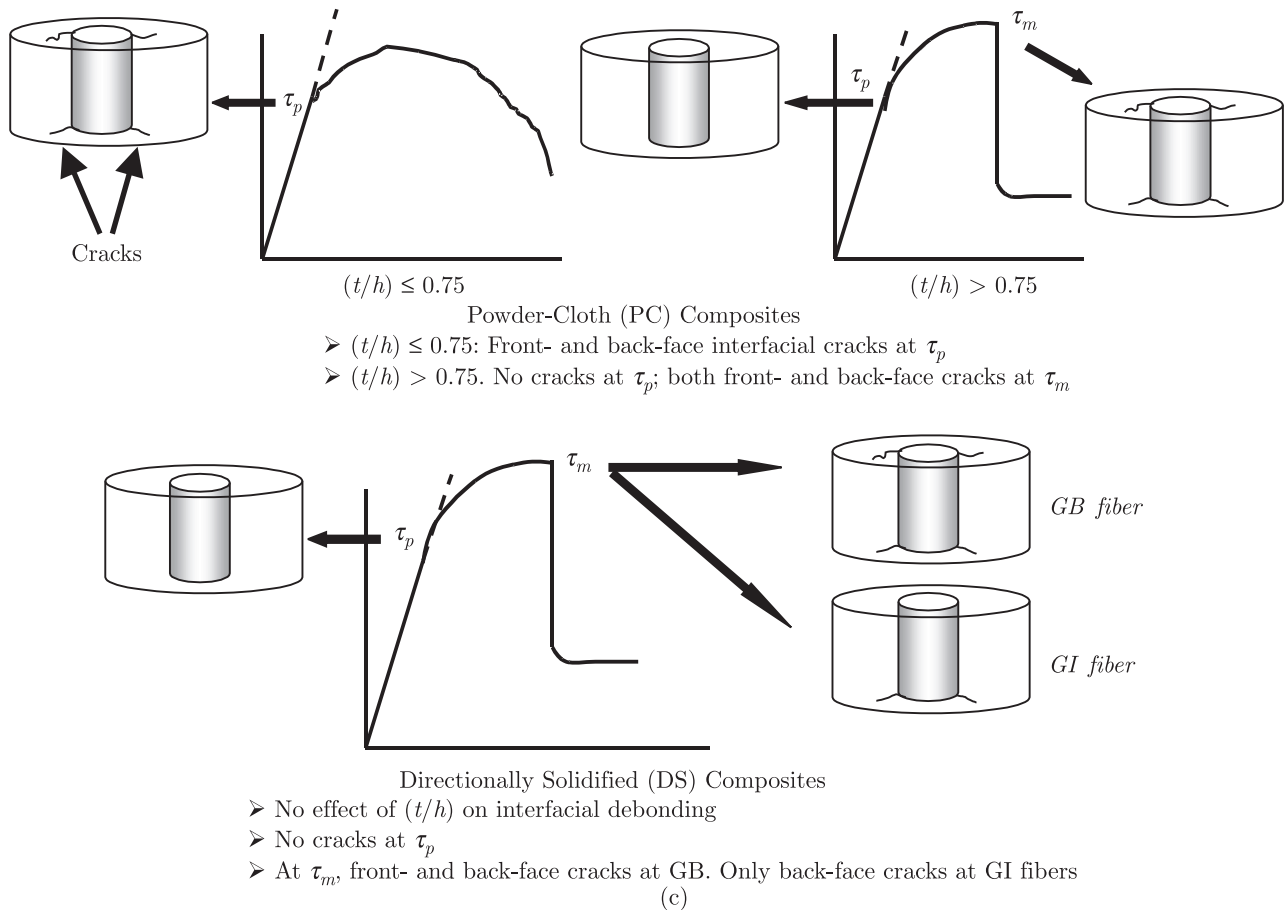


Fig. 9. The SEM views of fiber/matrix interfaces in NiAl/sapphire composites from interrupted fiber push-out test on thick and thin composite wafers. The push-out test was terminated at different stages of the loading process: (a) directionally solidified (DS) composites made from powder metallurgy (PM) feed stock with fibers either anchored at grain boundaries (GB fibers) or engulfed within the grain interior (GI fibers); (b) powder metallurgy (PM) composites; and (c) summary of the effect of disc thickness (t) and grain boundaries on cracking at τ_p and τ_m observed in different composite materials. The parameter, t/h , denotes the ratio of the wafer (or disc) thickness-to-support hole span width. Note that in spite of the interfacial porosity (Fig. 9(a)) from the binder residue, the shear strength was significantly higher for the GI fibers than for the GB fibers and for the fibers in the PM composites

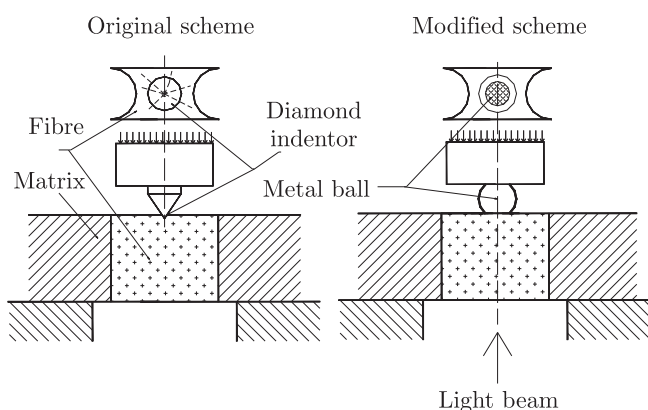


Fig. 10. A modified fiber push-out test that permits uniform loading of non-symmetrical fibers. The approach employs a ball indenter positioned between a flat-bottomed micro-indenter and the fiber; the ball indenter distributes the applied stress over a large area

fibers of a variable cross-section are encountered, such as those manufactured by ICM. The variability of fiber shape and size

could make it difficult to load a fiber exactly at its center of gravity, leading to fiber fracture or unreliable strength measurements. One approach to overcome this problem employs a metal ball indenter positioned between a flat-bottomed micro-indenter and the fiber [63]; the ball indenter distributes the applied stress over a larger area. Figure 10 shows a schematic illustration of the modified fiber push-out test.

5. Fiber-matrix interface strength

The room-temperature interface strength measurements in some Ni-base superalloys and intermetallics in contact with oxide ceramics are summarized in Table 2. The data in the Table need some commentaries. Besides the testing method and test configuration, processing conditions, binders, alloying, and interfacial coatings all influence the interface strength.

An example of the effect of processing conditions on interface strength is shown in Fig. 11. This figure shows the effect of pressure casting temperature on the interfacial shear strength in oxide fiber-reinforced Ni-base superalloy composites made

Table 2
 Interface strength in some nickel/oxide ceramic systems

System	Bond Strength, MPa	Technique	Reference
NiAl/sapphire (PC) ⁽¹⁾	50–150 (with binder), >280 (without binder)	Push-out	[30,64]
Ni ₃ Al/sapphire (cast)	19	Modified microhardness test	[70]
Ni ₃ Al-0.5Cr/sapphire (cast)	54.5	same	[70]
Ni ₃ Al-1Cr/sapphire (cast)	21.7	same	[70]
Ni ₃ Al-1Ti/sapphire (cast)	39.9	same	[70]
INCONEL 718/sapphire (cast)	>150	same	[21]
NiAl/Al ₂ O ₃	136±8	Push-out	[73]
NiAl/SiC-coated Al ₂ O ₃	107±10	Push-out	[73]
VKNA-4U ⁽²⁾ /Al ₂ O ₃ -YAG eutectic fiber (ICM)	5–100 (depending on wafer thickness, casting temperature and fiber volume fraction)	Modified push-out test with a ball indenter	[63]
GS-32 ⁽²⁾ /Al ₂ O ₃ -YAG eutectic fiber (ICM)	5–130 (depending on wafer thickness, casting temperature and fiber volume fraction)	Modified push-out test with a ball indenter	[63]
Ni/Al ₂ O ₃ (PC)	78	Improved droplet push-off shear test	[51]
Ni/Cr/Al ₂ O ₃ (PC)	138	Improved droplet push-off shear test	[51]
NiAl/sapphire ⁽³⁾ (DS)	138±62	Push-out	[59]
NiAl(Cr)/sapphire ⁽³⁾ (DS)	155±41	same	[67]
NiAl(W)/sapphire ⁽³⁾ (DS)	159±69	same	[67]
NiAl(Yb)/sapphire ⁽³⁾	205±69 (PC), 67±44 (DS)	same	[66]
Ni/Al ₂ O ₃ , Ni-Cr/Al ₂ O ₃ , Ni-Y/Al ₂ O ₃	71–111	Droplet push-off test	[35,39,52]

PC: Powder-Cloth (i.e., powder metallurgy or PM), DS: Directionally Solidified, ICM: Internal Crystallization Method

⁽¹⁾ weakly-bonded: PMMA (fiber binder), TEFLON (matrix binder), strongly-bonded composites did not have binders in them

⁽²⁾ Ni-base superalloys – the VKNA-4U matrix is Ni-8.5Al-4.8Cr-2.2Mo-3.9W-4.4Co-1.1Ti, and the GS-32 matrix is Ni-6.0Al-5.0Cr-1.0Mo-8.3W-4.0Ta-9.0Co-1.5Nb-4.0Re

⁽³⁾ average value of shear strength based on the fibers that could be pushed within the loading limit of the machine

using the ICM approach. The data are for Al₂O₃-GS-32 superalloy/Al₅Y₃O₁₂ composites containing 30% eutectic Al₂O₃-Al₅Y₃O₁₂ oxide fibers. The nominal composition of the GS-32 matrix is Ni-6.0Al-5.0Cr-1.0Mo-8.3W-4.0Ta-9.0Co-1.5Nb-4.0Re. The scatter in the shear strength data at a constant temperature is from the measurements made on composite wafers of different thicknesses. For the GS-32/Al₂O₃-YAG eutectic fiber composites, the interface strength is approximately 5–130 MPa depending on the wafer thickness. Similarly, the interface strength in another oxide fiber/Ni-base composite (VKNA-4U/Al₂O₃-YAG eutectic fiber composite) is in the range 5–100 MPa, and the interface strength in VKNA-4U/Al₂O₃ fiber composite is in the range 10–20 MPa (the VKNA-4U matrix is Ni-8.5Al-4.8Cr-2.2Mo-3.9W-4.4Co-1.1Ti).

The effect of binders can be illustrated from the example of β -NiAl/Al₂O₃ composites synthesized using a solid-state fabrication process (NASA's patented "Powder-Cloth" process). In the powder-cloth (PC) process, fiber mats are combined with plasma sprayed matrix powders through hot pressing. Polymethylmetacrylate (PMMA) is used as binder for fibers and polytetrafluoroethylene (TEFLON) is used as a base binder for NiAl matrix powders. Interface strength measurements on hot-pressed NiAl/sapphire composites using the fiber push-out test show [30,64] that composites containing PMMA and

TEFLON binders exhibit a purely frictional bond and low interface strength (50–150 MPa). Interface contamination from binder residues during hot pressing interfered with interface development; carbon (graphite) residue at the interface frequently served as fracture initiation site [65]. In contrast, interfaces in binder-less composites were chemically clean and possessed higher strength (>280 MPa) [64]; however, the problems of poor matrix ductility and mechanical damage to the fiber during hot processing have been major concerns.

The effect of alloying and fiber surface modification on interface strength can be illustrated by alluding to the behaviour of sapphire-reinforced NiAl. Titanium- and platinum-coated Al₂O₃ fibers bond strongly to NiAl in NiAl/Al₂O₃ composites. Titanium coatings also improve the bonding of Al₂O₃ fibers to Ni₃Al-matrix in Ni₃Al/Al₂O₃ composites (interface strength >150 MPa) when compared to composites made from uncoated fibers. Similarly, when uncoated Al₂O₃ fibers are incorporated in a NiAl matrix containing Zr, Y, Cr, Yb or W, the NiAl/Al₂O₃ bonding improves. Alloying additions such as Zr also strengthen the NiAl matrix (but Zr raises the ductile-to-brittle-transition temperature of NiAl). In a manner similar to NiAl, zirconium and yttrium additions to Ni₃Al also improve the bond strength to alumina, although Ti as an alloying addition to NiAl and Ni₃Al does not have a beneficial effect, and

low bond strength results (a similar situation is encountered in Al/Al₂O₃ couples where Ti coatings on alumina, but not Ti alloying of Al, markedly improves the bond strength [50]). Alloying NiAl with Cr, W and especially the rare-earth element, Yb, markedly enhances the fiber/matrix shear strength in NiAl/Al₂O₃ composites. The NiAl(Yb)/sapphire interface strength exceeds 205 MPa even when organic binders are used for composite fabrication, in contrast to 50–150 MPa in the absence of Yb alloying [66]. The extensive chemical interaction between the sapphire and Yb during processing roughens the fiber/matrix interface, increases the frictional shear stress (~53–126 MPa, depending upon the processing conditions), and causes stress undulations in the load-displacement profile during large-scale (frictional) sliding of debonded fibers during fiber push-out test. This behaviour is characteristic of other reactive fiber/matrix systems as well, such as the reactive Ti-48Al-2Cr-2Nb/sapphire composites.

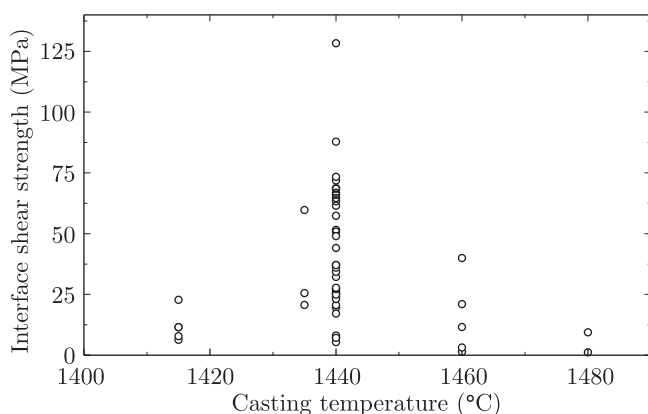


Fig. 11. The effect of pressure casting temperature on the fiber/matrix interface strength in a Ni-base superalloy/sapphire composite measured using a fiber push-out test apparatus that was modified for fibers of non-symmetrical cross-section. The scatter in the data at fixed casting temperatures is from the measurements on a range of wafer thickness

Alloying NiAl with chromium and tungsten has a beneficial effect on the Al₂O₃/NiAl bonding, with the interface strength in excess of 155 MPa [67]. The fiber/matrix chemical interactions are negligible with W alloying and no W-rich secondary phases preferentially segregate at the sapphire/NiAl interface. In the NiAl(Cr)/sapphire composites, however, the fiber/matrix interaction as well as preferential segregation of NiAl-Cr eutectic at the fiber/matrix interface during controlled solidification lead to high interfacial shear strength and high frictional shear stress. The NiAl(Cr) matrix exhibits wear tracks due to matrix abrasion by hard Cr particles during sliding of debonded fibers through the composite wafer in a fiber push-out test. The shear bond strength in NiAl(Cr)/sapphire composites is in the range of 114–196 MPa. Similar high bond strength (>150 MPa) is achieved in pressure cast sapphire/Inconel 718 superalloy composites [21] in which the fibers react with the active solutes in the composite matrix.

6. Chemical interactions and interface development

Chemical and structural changes during processing and service at the fiber/matrix interface are dictated by thermodynamics and their rates are limited by chemical kinetics. Hence, criteria for selecting the fiber and matrix materials for composites must consider the fiber's stability in and compatibility with the matrix over a wide range of temperatures and contact times. Many ceramic reinforcements rapidly degrade in reactive matrices during processing and service, although in most cases, judiciously selected coatings and barrier layers could reduce or eliminate the attack. Chemical interactions between the fiber and the matrix may also modify the properties of the fiber and the metallurgy of the matrix (e.g., age hardening response), and this must be considered when selecting the matrix chemistry. It should also be appreciated that a moderate level of chemical interaction between the fiber and the liquid matrix improves the wetting, assists liquid-phase fabrication, and enhances the interface strength, which in turn facilitates load transfer to the fiber. Thus, a careful balance between competing requirements is needed to create high-performance composite materials.

With reference to Ni-base composites, pure polycrystalline- and single-crystal alumina fibers such as sapphire are generally stable in Ni₃Al and NiAl matrices, and large-scale interdiffusion and reaction zones are normally not observed in diffusion-bonded and liquid-phase processed composites. Some local interdiffusion could, however, occur at high processing temperatures; for example, in Ni₃Al/Al₂O₃-fiber composites prepared by hot pressing at 1473–1553 K, the diffusion of Ni into fibers to a depth of ~400–500 nm is observed. Similarly, diffusion bonding of Ni₃Al/sapphire composites under high partial pressures of oxygen (poor vacuum) leads to Ni-spinel (NiAl₂O₄) and (Mg,Ni)-spinel (Mg,Ni)Al₂O₄ compound layers at the fiber/matrix interface [68,69]. No such interfacial reaction zones are observed between Ni₃Al and alumina when diffusion bonding is done under low partial pressures of oxygen (~2 × 10⁻⁴ Pa).

Whereas pure polycrystalline- and single crystal alumina is relatively stable in NiAl- and Ni₃Al- matrices, alloying elements, fiber coatings, and chemical impurities (e.g., sintering aids) in the fiber markedly alter the reactivity and cause structural changes (e.g., grain coarsening in the fiber). Thus, commercial zirconia-toughened alumina (ZTA) fibers (PRD-166) in a pressure cast Ni-45Al-1Ti matrix led to alumina grain coarsening, and rejection and dissolution of zirconia from the fiber into the metal [19,70]. Zirconium released from the dissolution of ZrO₂ chemically reduced and degraded the fibers. The PRD-166 fiber was also incorporated in a pressure cast Ni-base superalloy (composition: Ni-16.8Al-7.9Cr-1.2Ti-0.5Zr-0.1B, in at. %) [21]. The as-cast fiber/matrix interfaces were free of reaction products but showed coarse ZrO₂ particles. Pressure casting usually involves relatively short interaction times at elevated-temperatures, which reduces the extent of the fiber/matrix interaction.

In pure-sapphire-reinforced Ni₃Al-based γ'/γ alloys containing Cr, Mo, W, and Co, no visible trace of chemical in-

teraction is observed when the composites are fabricated using pressure casting [71], in which the interaction times at elevated temperatures are rather short. However, fibers of yttrium aluminum garnet (YAG) and YAG-alumina eutectic show some reactivity with the Ni_3Al -based γ'/γ alloy together with the formation of a new interfacial phase. Likewise, YAG fibers in a Ni-base superalloy containing (Re, Ta, W etc.) show interfacial carbides whereas pure alumina fibers show limited reactivity and only a very small amount of a new interphase. The fibers can be strongly bonded to the matrix as revealed by the interface strength measurements [71], which suggests the positive influence of yttrium of the fiber in promoting the interfacial bonding.

As mentioned earlier, another alloying element that exhibits marked reactivity with alumina is the rare-earth element ytterbium. Alumina is extremely unstable in Ni-alloys containing even small quantities of Yb; in sapphire-reinforced NiAl containing Yb, a strong reaction occurs because ytterbium oxide (Yb_2O_3) is more stable than Al_2O_3 , and sapphire

is reduced by ytterbium (the free energies of formation of Yb_2O_3 and Al_2O_3 are $-1727.5 \text{ kJmol}^{-1}$ and $-1583.1 \text{ kJmol}^{-1}$, respectively). A complex, multi-layer interface consisting of Yb_2O_3 and $\text{Yb}_3\text{Al}_5\text{O}_{12}$ forms in NiAl(Yb)/sapphire composites containing as low as 0.36 at. % Yb [66] (Fig. 12). Unlike Yb, chromium in NiAl only moderately attacks the sapphire; Cr preferentially precipitates on and bonds to the fibers. Reaction products do not form in Ni-Cr/ Al_2O_3 , and the improved bonding results from beneficial changes in the interfacial energy due mainly to adsorption of Cr-O clusters on alumina.

It should be mentioned that chemical reactions and interface development might be affected also by impurities. The most common impurity is Mg that might be introduced from the master alloy during its preparation. Moreover, during remelting of master matrix alloy and composite casting, Mg might come also from contacting refractory materials (crucibles, dies) containing MgO. Whatever the mechanism of the pollution of metal matrix with Mg, its presence results in the formation of interfacial Mg-rich spinel compound. Interest-

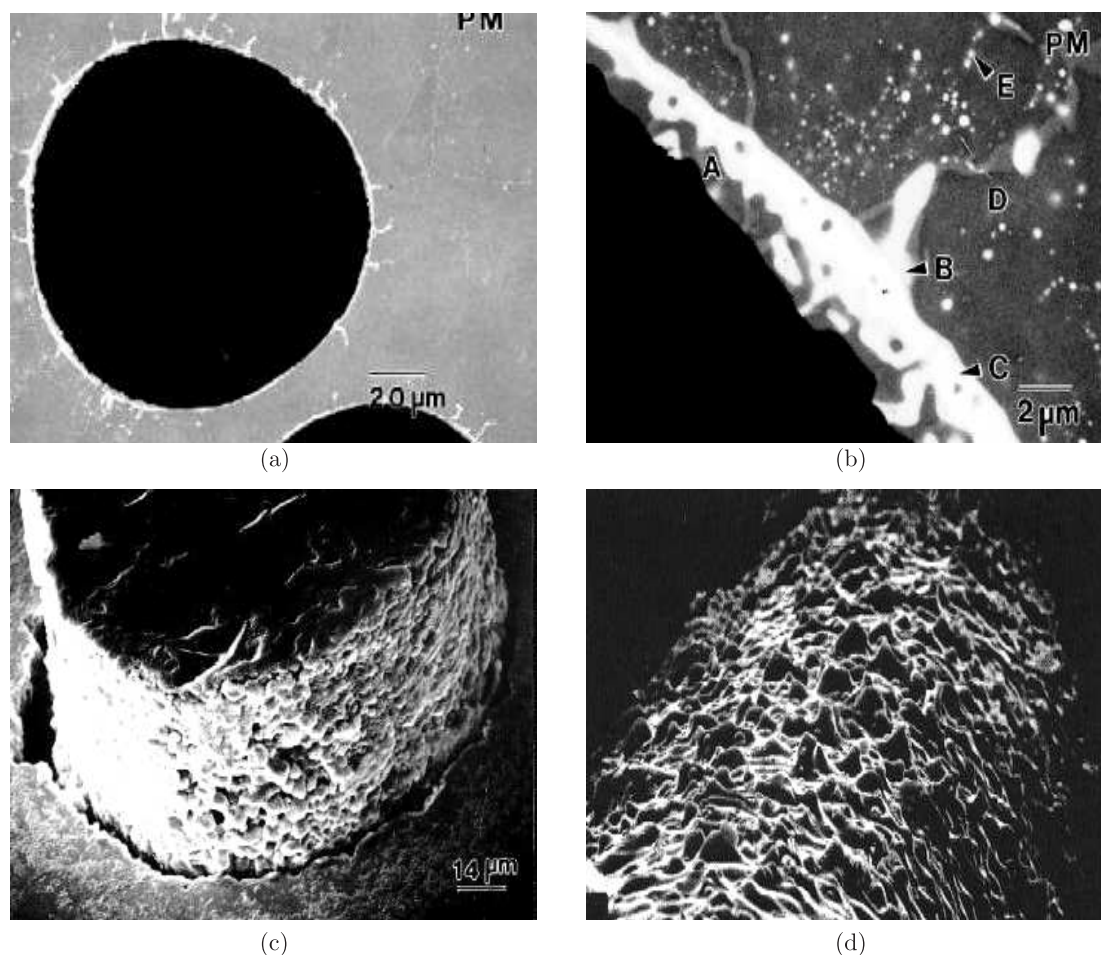


Fig. 12. SEM views of fiber/matrix interfaces in a NiAl(Yb)/sapphire composite (0.36 at. % Yb) showing reaction layer formation as identified in [66]: (a) powder-cloth composite, (b) a higher magnification view showing interface interphases: A- O-rich NiAl, B- $\text{Al}_2\text{O}_2\text{-Yb}_2\text{O}_3$ spinel ($\text{Yb}_3\text{Al}_5\text{O}_{12}$), C- Yb_2O_3 , D- NiAl matrix, and E- ytterbium fluoride (fluoride residue is from TEFLON binders used in the diffusion-bonded feedstock), (c) a partially pushed fiber in the NiAl(Yb)/sapphire composite wafer, and (d) surface appearance of a fiber extracted from the NiAl(Yb) matrix showing extensive surface reconstruction from the chemical attack

ingly, during the sessile-drop wettability test under protective atmosphere, Mg easily evaporates and its vapor reacts with oxide-containing ceramics to form the same Mg-rich spinel compound in the form of long whiskers, growing from the interface around the drop [76]. This phenomenon results in the substrate surface roughening and drop pinning, both contributing to apparent contact angle values and possibly modifying the drop/substrate interface strength.

Chemical interactions resulting from deliberate matrix alloying or inadvertent impurities released into the matrix affect not only the wettability and interface strength but also the strength of the reinforcing fibers themselves. Single-crystal sapphire fibers extracted from Ni-base superalloy matrix composites are known to experience 45–65% strength loss based on tests conducted on isolated fibers outside the matrix, and the probability of fiber failure is generally consistent with the Weibull distribution function. The strength loss has been attributed to the formation of brittle reaction product layers at the interface. A high interface strength from chemical reactions achieved at the expense of fiber surface quality and fiber strength is generally considered undesirable for creep-resistance at elevated temperatures. Recent studies [12,18], however, have examined this problem carefully and they show that it should be possible to design composite microstructure with high creep-resistance even when fiber surface reconstruction and morphological changes from chemical interactions somewhat degrade the strength of the fibers extracted from the matrix and tested outside the matrix. Of central importance to this somewhat unorthodox idea is the need to optimize the composite microstructure. The fiber/matrix interactions yield, indeed, defects in the fiber surface. But these reaction-formed defects as well as any original surface defects in the virgin fiber can be healed by the matrix material (or by judiciously selected coatings such as carbides or carbon) so that the fiber residing in the matrix will exhibit diminished sensitivity to surface defects as compared to a fiber extracted from the matrix and tested outside the matrix. The effective fiber strength that determines the composite strength is higher than the strength of separate fibers if the fiber/matrix interface is able to heal surface defects on the fiber. The situation is analyzed in detail in [12,18].

7. Interface design for creep resistance

The creep-resistance of Ni-base composites is of considerable technological importance from the standpoint of heat-resistant applications. The creep-resistance of fibrous composites depends on the interface strength, which in turn, depends upon the composition of both constituents, fabrication technology, and process and structural parameters. In addition, real materials in structural elements experience temporally varying loading. The composites of a given type can experience diminishing interface strength as a result of cyclic loading; the lower the interface strength, the quicker is the decrease in the interface strength with cycling provided all other conditions are the same. This will also influence the composite's creep behaviour.

The fiber/matrix interface strength in a composite depends also on the fiber volume fraction, a fact that is not always read-

ily appreciated. However, independent of reasons for fiber volume fraction to affect the interface strength, such behaviour of the composite provides an opportunity to scientifically evaluate the dependence of creep-resistance on interface strength. To justify the procedure to explain the creep behaviour of composites with the interface strength varying with fiber volume fraction, experimental results on creep-resistance and interface strength must be analyzed. Recent studies [12,18] at the Solid State Physics Institute of the Russian Academy of Sciences on mechanics and microstructure of the composites show that the effective fiber strength that determines composite strength is higher than the strength of separate fibers if the surrounding matrix (or a coating) is able to partially heal the fiber surface defects, thereby diminishing the deleterious influence of the flaw on the fiber strength. These studies have revealed a synergistic role of the fiber/matrix interface in determining the composite's creep-resistance. The results highlight an essential role of the "quality" of the fiber/matrix interface in designing the composites with creep-resistance.

The creep behaviour of the composites predicted by the theoretical micromechanical models for fibrous composites [12] is closely related to the real behaviour provided parameters of the models are accepted. For example, the first approximations to the strength characteristics of the fiber and creep characteristics of the matrix are taken from independent measurements. In a recent theoretical model, a parameter, α , characteristic of interface strength, is defined. It is taken as the ratio of average interface strength at room temperature (~ 15 MPa) to the room temperature strength of the matrix alloy (~ 700 MPa). The parameter, α , has been systematically varied in composites by judiciously selecting the matrix. In particular, very weakly bonded composites ($\alpha = 0.005$) based on Ni_3Al , moderately bonded composites ($\alpha = 0.05$) based on a modified Ni-Al alloy, and ideally-bonded ($\alpha = 1$) composites based on TiAl- or Mo-based matrices (both of which are wetted by oxide melts) have been investigated for creep-resistance and interface strength in oxide fiber-reinforced composites. TiAl matrix is chosen for its ideal bond strength, which has not been reached yet in composites with Ni-based matrices (the largest present value of α for Ni-based matrices is 0.5 that corresponds to an intermediate range of values of fiber strength). On a positive note, however, the creep data for Ni-based composites relate to higher temperatures of 1423–1473 K, which shows the technological potential of these composites.

The creep model parameters are varied over a narrow range to adjust the calculated dependencies to experimental points. These adjustments are needed, as the constituent's characteristics in the composites are different from those determined outside the composite. Recently developed creep models [12] provide a good description of the experimental data over a rather large interval (four orders of magnitude) of the creep rates. The models yield the correct dependence of composite stress on creep rate, and include statistical characteristic of the fiber strength and creep characteristics of the matrix, a parameter that characterizes the continuity of the interface, and the factor, α , describing the fibre/matrix interface strength, mentioned above.

It is important to point out that the creep-resistance/fiber volume-fraction dependence is non-monotonic in composites, and the maximum corresponds to the fiber volume fraction at which the interface strength starts to decrease. A hypothesis can be formulated to explain why the interface strength is small at high fiber volume fraction in a particular matrix, but at small values of α ($\alpha = 0.01$, $v_f > 0.25$), the creep-resistance is described by a model that includes the fiber strength values obtained by testing separate (i.e., extracted) fibers, outside of the composite matrix. For a limiting value $\alpha = 1$ (ideal bonding), a maximum effective fiber strength is reached. A detailed exposition of the role of the interfacial parameters in designing creep-resistant fiber-reinforced Ni-base composites will be presented in a separate paper [72].

8. Summary and conclusions

Oxide fibers such as sapphire have long been considered as potential reinforcement materials for nickel-base matrices for heat-resistance applications. After nearly three decades of active research, however, interest in these materials began to wane in mid-1990's due chiefly to 1) a lack of single-crystal oxide fibers sufficiently cheap to be used in structural composites, and 2) fiber strength loss during processing due to chemical interactions with reactive solutes in Ni-base matrices. At the present time, the cost disadvantage has been mitigated by the development of Internal Crystallization Method (ICM) of fiber growth that produces monocrystalline oxide fibers in a cost-effective manner. The decline in interest in the Ni-base/ Al_2O_3 composites after initial observations of strength loss in extracted fibers slowed the technological development of these materials. Recent research has shown that it is possible to design the composite microstructure with adequate creep-resistance even when fiber surface reconstruction from chemical interactions may have degraded the strength of the fibers extracted from the matrix and tested outside the matrix. Of central importance to the implementation of this somewhat unorthodox idea is the need to optimize the composite- and fiber/matrix interface microstructure so that reaction-formed defects and any original surface defects in the fiber may be healed by the matrix (or by a suitable coating material). As a result, a fiber residing in the matrix may exhibit diminished sensitivity to surface flaws as compared to fibers extracted from the matrix and tested in isolation of the matrix. Generally, the Ni-base/ Al_2O_3 composites exhibit acceptable levels of wettability and interface strength (further improved with the aid of reactive solutes and surface coatings), and show promise of elevated-temperature creep-resistance. Thus, in order to develop Ni-matrix/oxide fiber composites for heat-resistance applications, the quality of the interface (wettability, chemical make-up, defect content, and interphase morphology) is of considerable technological importance. In this paper, we identified several key issues related to the measurements of wettability (contact angle), interface strength, and chemical and structural transformations during processing at the fiber/matrix interface. There should be no doubt that optimization of the interface- and composite microstructure through

judicious control of processing and surface engineering shall yield promising Ni-base/oxide-fiber composites.

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