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Review article

An overview of ceramic molds for investment casting of nickel superalloys

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ABSTRACT

Accelerating advancements in technological systems have demonstrated a need for alloys with drastically improved thermomechanical and chemical properties, called superalloys. Ceramic molds are typically used in near-net shape investment casting processes of superalloy components due to their chemical inertness and high-temperature capabilities. Ceramic molds, however, often suffer from shortcomings in vital properties including flexural strength, thermal shock resistance, permeability, dimensional stability, corrosion resistance, and leachability, which have restricted their ability to adequately process modern alloy castings. This study analyses these limitations and illustrates how to address them, particularly regarding ceramic mold and slurry design, processing of shells and cores, material selection, and testing and characterization. By utilizing advanced processing methods including additive manufacturing and gel-casting, more dimensionally accurate and preferentially built molds can be formed. Additionally, by varying the mold composition to achieve more chemically inert structures, reactions with the mold can be mitigated to reduce chemically induced defects.

1. Introduction

A constant driving force behind the advancement of the metallurgical industry has been a desire for enhanced properties that allow metallic components to tolerate the extreme thermal, mechanical, and corrosive stresses imposed by many state-of-the-art engineering systems. At the forefront of modern metallurgical technology are superalloys, which are critical to the operation of several contemporary systems such as nuclear plants as well as commercial and military engine turbines due to their superior mechanical strength and fatigue properties as well as their chemical and thermal stability [1]. This is accomplished in large part by preferentially utilizing processing techniques to control the microstructure and composition of the alloy. Mechanical properties can be heavily influenced in this way by changes in grain size, grain boundaries, porosity, precipitates, and phase manipulation [2–5].

For the purpose of this review, we will refer primarily to aerospace turbine engines. These systems operate in thermally and chemically demanding environments and components such as turbine blades are susceptible to failure due to creep, oxidation, or fatigue as they are subjected to high-temperature stresses for thousands of hours during operation [6–8]. In aerospace applications in particular, superalloys are required for peak performance as increased operating temperatures—often reaching the range of 1400–1500 °C in turbine sections—directly correlate with engine efficiency [9–11]. As such, widespread

implementation of superalloys for high-efficiency engine components represents, in addition to cost-effectiveness, a promising mechanism to mitigate harmful greenhouse gas emissions which threaten global climate and public health [12,13]. For instance, according to the International Civil Aviation Organization, airplanes have accounted for a net 500 megatons in CO₂ emissions, a number which could triple by 2045 [14]. While economically beneficial, however, these elevated temperatures also exacerbate the aforementioned failure mechanisms of turbine components. For this reason, improved processing techniques are required in order to efficiently produce components capable of withstanding these phenomena at further increased operating temperatures.

Investment casting is essential as a method to produce near-net shape turbine blades due to the complexity and high-volume production of these parts. Use of ceramic cores during casting allows for the added benefit of control over internal geometries necessary to introduce cooling schemes which permit the engine components to operate at temperatures higher than the melting temperature of the alloy for enhanced engine efficiency [15,16]. Furthermore, this casting technique is capable of governing microstructural characteristics through directional solidification (Fig. 1), a process by which single crystal blades are formed with improved high-temperature strength and oxidation resistance [1,17,18]. These single crystal blades are valuable to avoid grain boundaries normal to the axis of stress application, which account for most of the thermomechanical damage that occurs in polycrystalline

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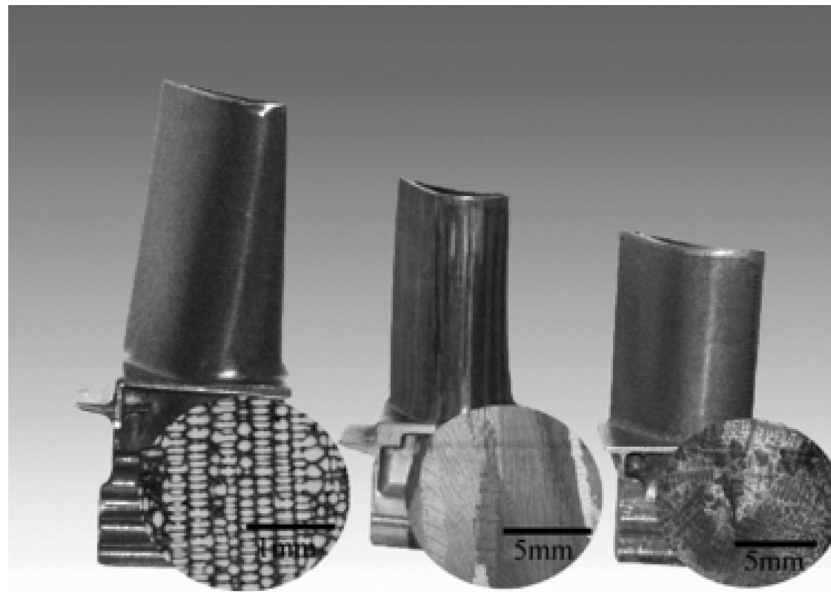


Fig. 1. Grain structures of (from left-to-right) single-crystal, directionally-solidified, and conventionally-cast turbine blades (reprinted with permission from Ref. [11]).

crystals [19].

Investment casting is a technique, as shown in Fig. 2, during which a wax pattern is coated with a refractory ceramic slurry, stuccoed, and allowed to dry in a repeating layering process to form a set of ceramic molds (Fig. 3). The wax is subsequently melted from the mold to form a cavity and the green ceramic component is fired to yield a sintered mold with sufficient mechanical strength. A molten alloy can then be poured into the cavity where it solidifies to form a cast component. Once solidified, the mold undergoes divesting during which it is removed from the casting by mechanical or chemical means. Finally, the casting is subjected to finishing processes to finalize the component

[20].

Casting of modern alloys, while historically effective, presents its own set of unique challenges. A major challenge is the tendency of alloying elements to react in varying degrees with traditional ceramic mold materials such as alumina, zircon, and silica [21]. These reactions subsequently produce an undesirable reaction layer on the surface, for instance, by drawing active elements from the solidifying melt and allowing for diffusion at the ceramic interface, altering the elemental composition in the bulk of the alloy [22]. Further research indicates that surface scale comprised of oxides of active elements forms only when intimate contact is lost between the mold and metal and an initial

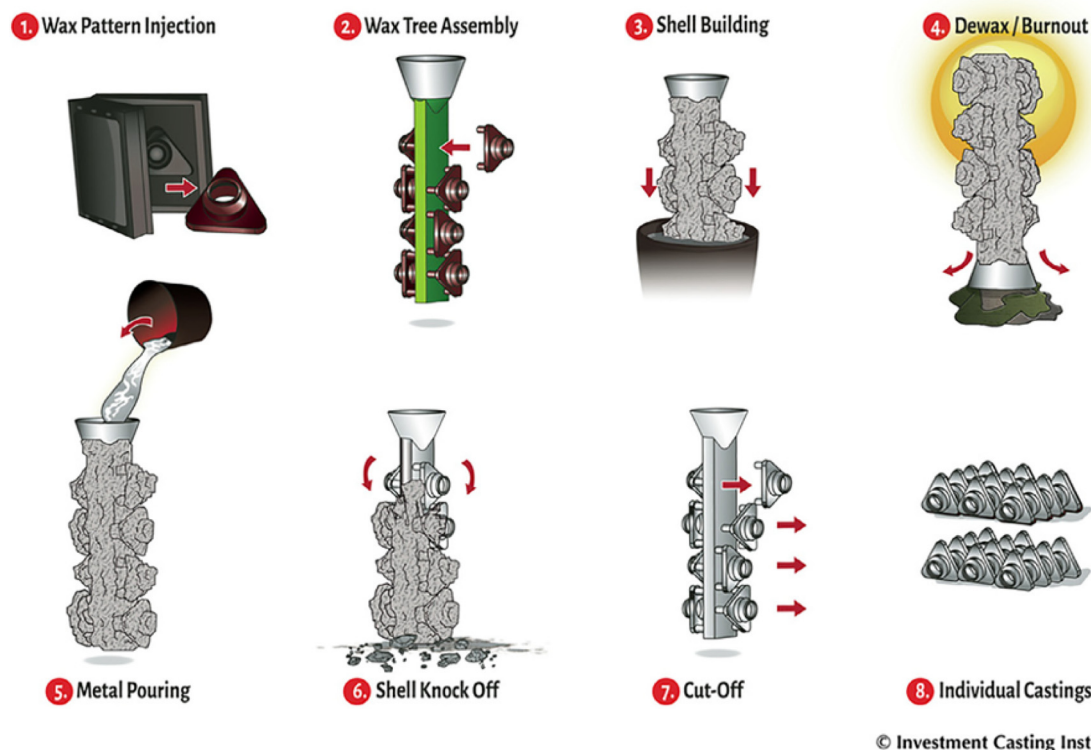


Fig. 2. Basic steps involved in ceramic shell investment casting (reprinted with permission from Ref. [26]).

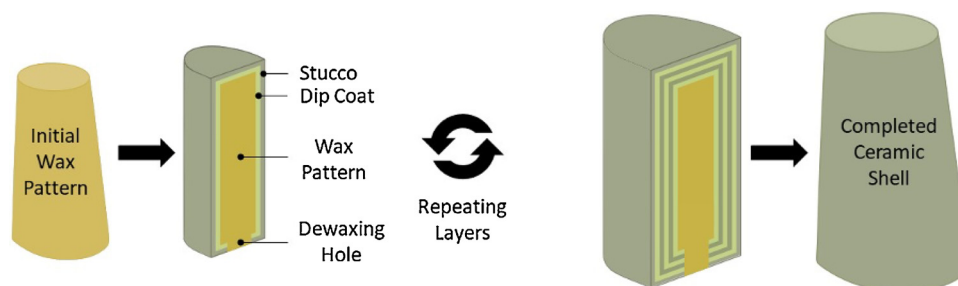


Fig. 3. Schematic representation of the dipping and stuccoing process, repeated to form a layered shell over a wax pattern.

protective alumina coating generated by the Al in the alloy is lost, leaving the bare melt vulnerable to oxidation [23]. Mitigating the aforementioned chemical reactions between the ceramic and the melt significantly improves component life and minimizes failure potential. Moreover, traditional methods of casting have been limited by the mechanical properties of their ceramic components, with both excess mold fragility and rigidity often resulting in casting defects in the form of dimensional and/or structural flaws upon interaction with the solidifying alloy melt [24]. Finally, dimensional parameters of the ceramic mold are often difficult to meet, with more intricate internal geometries unable to be produced within acceptable casting tolerances [9] and distortion occurring during manufacturing [25].

In this review, compelling ceramic materials as well as principal processing methods of ceramic investment casting molds are analyzed to discuss the state-of-the-art and address future prospects revolving around the issues presented by the investment casting of nickel superalloys. The review is divided into five main parts: (i) ceramic mold and slurry design; (ii) processing of ceramic shells and cores; (iii) ceramic materials; (iv) testing and characterization of molds; (v) future prospects and overview.

2. Design of ceramic slurry and mold

There are several critical properties that must be considered in the design of ceramic investment casting shells and cores that are crucial to the formation of near-net shape, intricate components. Some major requirements of the ceramic mold include having sufficient strength to withstand induced forces from the cast alloy during solidification, thermal stability for dimensional accuracy, and a mechanism of complete removal for the core material after solidification of the alloy [24]. The mold must additionally exhibit a low reactivity with the alloying elements found in the alloy as well as open porosity to promote sufficient air permeability. Furthermore, high thermal conductivity is desirable to allow for adequate cooling of the cast metal through the ceramic wall [27].

This cooling of the superalloy is a focus of mold design, not only during the solidification process but also during cast component operation as well. In the case of turbine components commonly generated through investment casting, operating temperatures can reach values approaching or above the melting temperature of even nickel superalloys in order to boost engine efficiency, as explained previously [24]. Because of this, airfoils are required to contain intricate interior cooling passages. These passageways are generated through the use of ceramic cores which form internal cavities to circulate compressed air (Fig. 4), moderating the temperature of turbine components from the temperature of the engine environment to a level below their maximum use temperature [28,29].

It is possible to make significant improvements to the properties of a ceramic mold by directly altering the ceramic slurry prior to the investment casting process. This includes changes to viscosity, density, binder, filler/sol ratio, wetting agents and antifoaming agents [30]. Many of the more recent advances have come through additives and fillers which can be independently controlled and have a significant

effect on the performance of the fired mold. For example, in order to increase the permeability, sacrificial pore forming agents (PFAs) can be added to the ceramic slurry prior to forming the shell [31]. Common PFAs include organic materials such as carbon, rice husk, walnut shell, seeds, and various polymers as well as inorganic compounds such as ammonium carbonate. During firing, these additions are burned out, drastically increasing shell permeability. Unfortunately, this permeability typically comes at the cost of shell strength, reducing the load bearing capacity of the mold. The problem of diminished shell strength is exacerbated at corners and leading edges of the mold design where the thickness of the shell is smaller than at flat sections due to reduced surface area [32]. The surface area decrease leads to a reduction in stucco volume density at these edges (Fig. 5), increasing the probability of crack propagation in already stress-concentrated areas of the mold [33,34].

Compensations to diminished green and fired shell strength have commonly been made by adding more layers to form a thicker shell, however excess coating counteracts the sacrificial pore process to result in decreased permeability, cooling rate, and collapsibility [35]. Collapsibility describes the ability of the mold to give way during thermal contraction of the casting and is an important factor to prevent defects from forming in the mold during cooling of the solidified alloy. These defects can occur as a result of shrinkage of the alloy relative to a ceramic, which is expanding due to positive heat transfer from the alloy [36]. In the core, this opposing motion limits natural contraction of the alloy and induces stresses that can cause cracking and distortions, particularly in alloys with a relatively low fracture toughness and ductility such as titanium alloys [37]. A collapsible core avoids these defects by giving way under sufficient force, allowing the alloy to shrink freely after sufficient solidification has occurred to maintain its shape independently of the mold.

A similar phenomena can occur in a shell in concave areas where the ceramic shell inserts into a casting, however convex ceramic shells cause a separate issue as a result of expansion. Fig. 6 shows the effect of thermal displacement during the initial stages of solidification for an aluminum alloy. As can be seen, the opposing thermal deformation can result in loss of contact between the mold and metal and, in turn, a reduction in heat transfer [36,38,39]. For this reason, molds are commonly preheated to a temperature approaching the melting point of the alloy to limit the thermal expansion and mitigate the formation of gaps at the mold-metal interface. Additionally, mold preheat reduces thermal shock effects and increases the fluidity of the melt by reducing the thermal gradient between the melt and mold, allowing improved melt flow into the mold cavity [40,41]. For the processing of nickel superalloys, these effects are typically achieved through preheat temperatures of around 1000–1250 °C [8,42].

Permeability is also a critical factor in mold design, as it allows for gas expulsion during mold filling. Prior to casting, the mold cavity is filled with air or inert gases such as argon. As it is displaced by molten metal during pouring, it is essential that the existing gas is rapidly expelled from the mold in order to prevent remnant gaseous bubbles or backpressure. These phenomena inhibit the flow of the metal and often result in areas of defect and non-fill, compromising the structure and

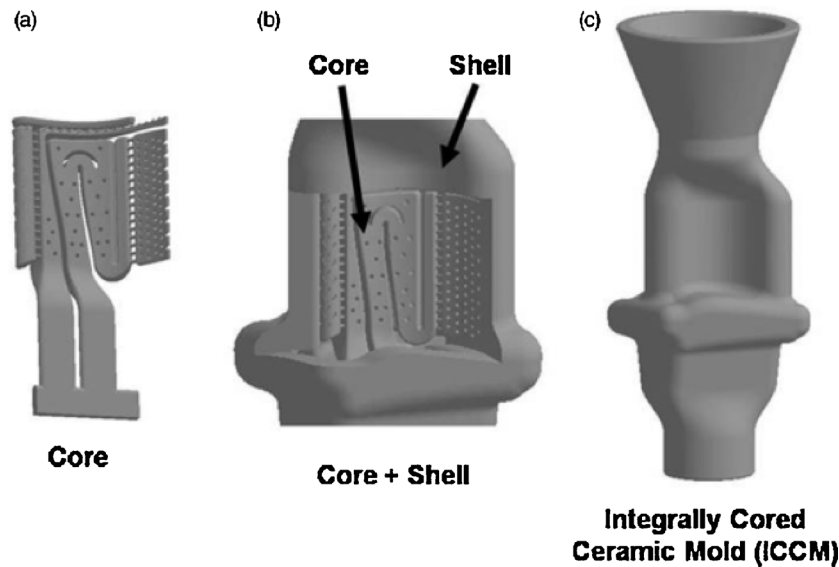


Fig. 4. Mold design for turbine airfoil, including (a) ceramic core for internal passageways, (b) cross-section of mold, (c) external design of integrally-cored mold (reprinted with permission from Ref. [28]).

morphology of the component [27]. To improve the shell strength without adding layers, efforts were made to alter the ceramic slurry itself by adding a latex-based liquid polymer to the binder. While this modification has successfully led to improved green strengths, the liquid polymer addition is cost-limiting and burns out during the firing phase, reducing the fired strength of the mold [33].

Consequently, several efforts have been made to develop fiber-modified ceramic molds in order to produce molds with sufficient strength and permeability without the need for liquid polymer additions [32]. Initial advancements were made when organic fiber additions, including nylon, were used to improve mold strength to cast aluminum alloys [43]. Using these nylon fibers, adjusted fracture load (AFL) bearing capacity was increased by 86% from that of the liquid polymer modified binder system while still maintaining sufficient flat mold strength. The AFL is a measure of load bearing capability before fracture for a normalised sample with a width of 10 mm across a 70 mm span. Compared to the latex modified binder, the thickness of the shell was also increased by 15%, with a 50% thickness increase displayed at mold edges [32,44]. Furthermore, the burnout of the fibers during firing also provided an added benefit of increased shell permeability (Fig. 7) to allow for more rapid and complete transport of gas through the mold to avoid gaseous defects in the cast metal during solidification. This was supported through alternative natural fibers as well, when cattail fibers (natural fibers extracted and spun from the cattail plant) were shown to improve green bending strength by 44% at just

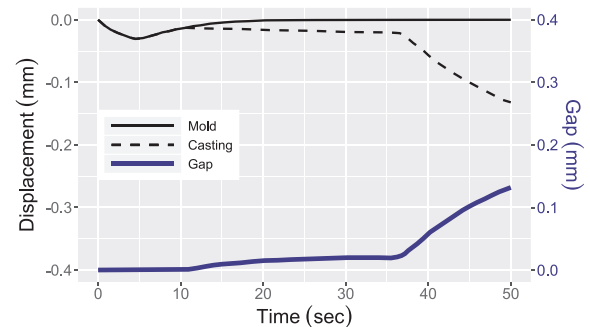


Fig. 6. An example of the displacement curves of the casting and mold at the center nodes of mold-casting interface (redrawn with permission from Ref. [38]).

1.0 wt% addition without significant drop to sintered strength despite increased permeability. This favorable post-firing strength is attributed to microholes left behind after burnout, which inhibit crack propagation [45].

Though these fiber-modified slurries represented a massive step for ceramic molds, some shortcomings were noted that still detrimentally affected the slurries. Traditional pore-forming fiber methods had difficulty providing a simultaneous increase to both fired strength and

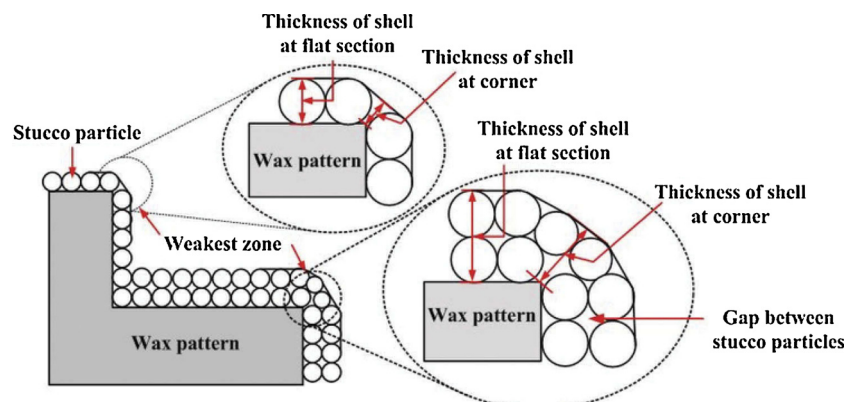


Fig. 5. Illustration of surface retention of along flat sections and sharp edges (reprinted with permission from Ref. [33]).

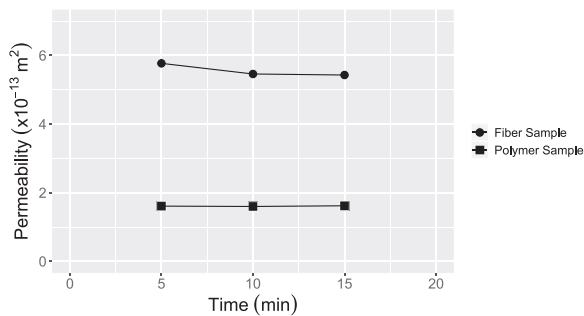


Fig. 7. Comparison of mold permeability tested at 800 °C for fired polymer-modified and fiber-modified samples (redrawn with permission from Ref. [32]).

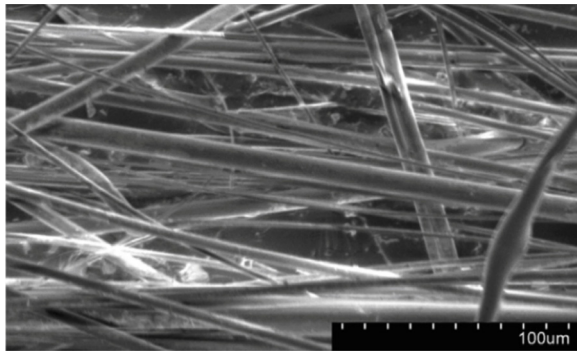


Fig. 8. SEM image of aluminum silicate fiber (reprinted with permission from Ref. [35]).

permeability. This is because strengthening during sintering occurs as a result of reduction in intergranular distance, implying an intrinsic inverse correlation between the two properties [46]. Furthermore, the fibers were also often difficult to keep dispersed in the slurry and made accurately measuring the slurry viscosity more difficult. More significantly, they tended to reduce the accurate contact to the wax pattern, making reproduction of more intricate details more complicated [47]. Additional research supported this, adding that the smooth surface topography of the fibers makes them susceptible to pull-out, compromising the strength of the shell [33]. A hybrid fiber of aluminum silicate and polypropylene was found to have the capability to simultaneously increase green strength, fired strength, and shell permeability [35]. Many of the aforementioned limitations of the pore-forming fiber-reinforced matrices such as pulling out of the fibers, however, do still apply to the fibers. Additionally, it has proven difficult to control the orientation of the fibers (Fig. 8). This becomes problematic when the pores left behind by the ablation of the fibers are parallel to the fracture surface, when they can act as mechanisms of crack initiation [33].

In an attempt to address these limitations of fiber additions, many recent studies have investigated replacing fiber reinforcements with powder additives. Unfortunately, literature indicates that it is very difficult to enhance both permeability and flexural strength by using a single ingredient as improvements to one often come at a detriment to the other. A method to circumvent this phenomena is to utilize a hybrid mixture of nano alumina, a strength increasing modifier, and particulate camphor, a permeability increasing modifier, as counterbalancing agents to improve both properties from a conventional slurry. It was found that by using a modified ceramic shell with a hybrid mixture, it is possible to simultaneously increase the hot permeability (Fig. 9), load bearing capacity (Fig. 10), and corner strength when compared to a conventional slurry [33].

Alternatively, several researchers have made progress by utilizing fiber additions which do not burn out during firing, such as zirconia. As expected, zirconia fibers in an alumina matrix were shown to improve

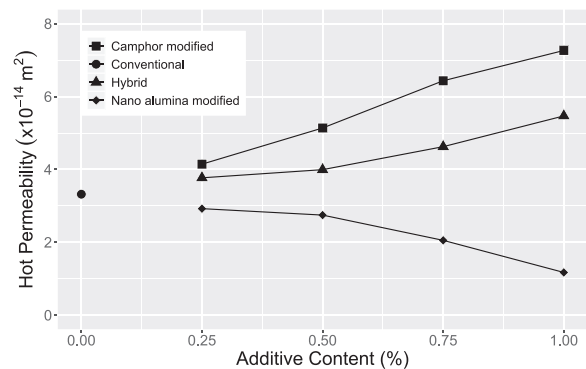


Fig. 9. Hot permeability of respective shell compositions with increasing additive content. Camphor used as pore-forming agent to counteract increases to shell thickness resulting from nano alumina additions (redrawn with permission from Ref. [33]).

bending strength by up to 261% through aforementioned fiber-reinforcement mechanisms [46]. Interestingly, however, the fiber additions also improved the porosity of the structure, achieving over 27% open porosity despite the fibers not burning out during firing. This is attributed to the interlocking fiber network which has been shown to induce a well-connected pore structure, likely due to pore distribution around the fibrous network improving pore connectivity [46,48,49].

Another compositional factor which has a large influence over the green and sintered properties of a ceramic mold is the binder content. The primary role of the binder is to provide sufficient green strength for the unsintered mold to undergo initial processing steps, however it can also have a large impact on several properties of ceramic shells and cores including viscosity, stability, and sintered permeability. One of the primary binders used in ceramic slurries is colloidal silica, which replaced ethyl silicate binders due to governmental regulations [50,34]. This is because colloidal silica can offer sufficient green strength and stabilizes the slurry to avoid self-gelation and agglomeration [51,52]. It has been found through several studies that the properties can be heavily impacted by various parameters of the silica binder, including solid fraction and filler to binder ratio. For increasing silica content, viscosity has been shown to increase appreciably (Fig. 11), resulting in increased bending strength and decreased permeability [52,53]. This is because during the drying process, the silica particles gel form a network of siloxane bonds [54]. This process can be accelerated by electrolyte additions, which neutralize the silica particles and decrease drying time [53]. In a similar manner to solid fraction, increased filler to binder ratio increases the density of the slurry and as such, the viscosity and bending strength of the resulting shell [53].

In addition to the traditional colloidal binders, a more recently emphasized generation of water-soluble binders also shows promise to create mechanically viable ceramic molds. One of the most commonly investigated water-soluble binders is polyvinyl alcohol (PVA), an organic polymeric binder which has been shown to increase both viscosity (Fig. 12) and bending strength with increasing content [55,56]. Another study supported this, further comparing PVA to two polyacrylic binders in a silicon carbide ceramic system with 20% (PA) and 40% (PA2) mass fractions vinyl acrylic copolymer respectively. This study found that at 15 wt% binder, the PA binder offered the more desirable combination of properties. These properties included relatively low viscosity as well as the best adhesion and stability [50]. More investigation is necessary into the parameters of the slurry system relative to water-soluble binders and how they can be altered to influence specific properties of the ceramic mold.

3. Processing

Investment casting is a classic method of metal processing, the basis

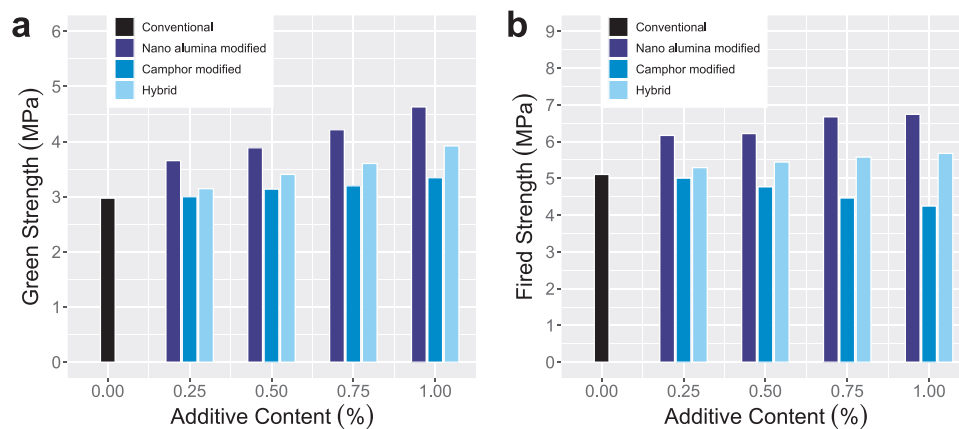


Fig. 10. Flexural strengths of (a) green shell and (b) fired shell for respective shell compositions. Strength increases result primarily from improvements to shell thickness, particularly at edges (redrawn with permission from Ref. [33]).

of which has remained steady even through vast advancements in materials technology. The classical technique of “lost wax” casting dates back millennia and has remained prevalent even in modern times due to its low cost, dimensional accuracy, and repeatability. As such, slurry-dipping techniques generally remain a primary method of processing ceramic shells for investment casting. The development of more intricate systems and precise specifications of cast components, including modern turbine airfoils, necessitated investment casting molds to include ceramic cores as well. These cores help form internal geometries for a variety of reasons, primarily the addition of cooling passageways for temperature control [1]. The processing of these cores has likewise been rather constant since its inception, with injection molding acting as the dominant forming method. Unfortunately, the extreme demands of superalloy casting intensify many of the aforementioned limitations that exist with conventional molds, in particular the limited control over the structural characteristics which may affect mechanical and thermal properties as well as interface reactions between melt and the ceramic mold.

3.1. Barriers

Nickel superalloys contain various alloying elements, such as Ti, Co, Hf, C, W, Ta, Re, Al, Y, Cr, Zr, Mo, and B. These additives can influence physical transformations through the suppression and/or stabilization of varying phases in order to improve the thermomechanical and chemical performance of the alloys [3–5]. For instance, hafnium is added in quantities less than 1% to improve the creep resistance of nickel alloys and slow microcrack initiation and propagation during solidification [57]. Additionally, elements such as Cr and Al offer improved corrosion resistance while C and Y can reinforce grain boundaries to

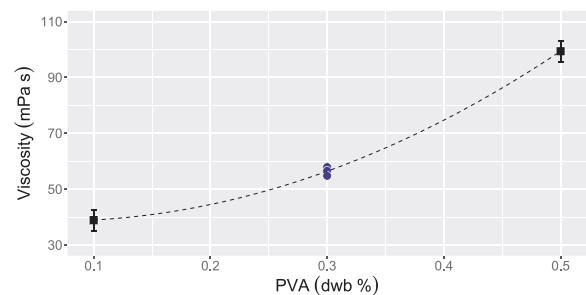


Fig. 12. Effect of with polyvinyl alcohol (PVA) content onto viscosity, showing an increase in viscosity as PVA content increases (redrawn with permission from Ref. [55]).

improve mechanical strength of polycrystalline alloys [58,59]. While these elements, as well as several others previously mentioned, are critical to the function of the alloys, they have also been shown to aggravate interfacial reactions with ceramic molds during casting [21,60–62]. These layers, amongst other disadvantages, significantly increase processing costs and reduce dimensional accuracy of the casting. As such, mitigation of these chemical reactions during casting is a crucial step to the formation of more precise and cost effective molds.

A widely adopted method to reduce interface reactions is the application of face coats as inert barriers on the outer surface of the core and inner surface of the shell. The barriers, usually comprised of metal oxides, nitrides, carbides, and/or silicides, are applied to reduce the diffusion of ions from the ceramic material into the alloy by forming a non-reactive surface to alleviate defects that result from chemical

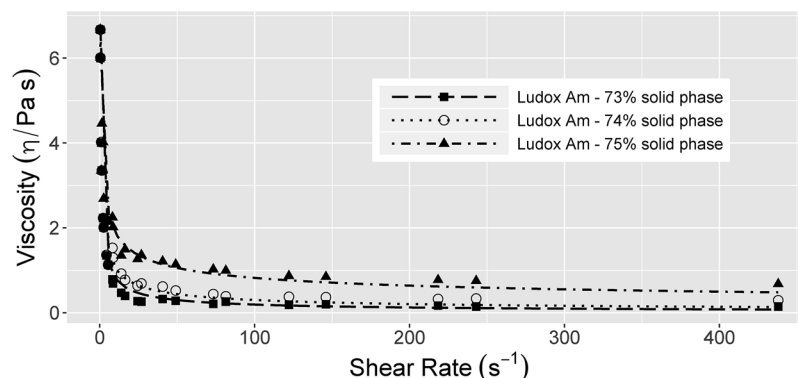


Fig. 11. Effect of wt% solid phase of colloidal silica binder on slurry viscosity, showing an increase in viscosity as solid phase silica increases (redrawn with permission from Ref. [52]).

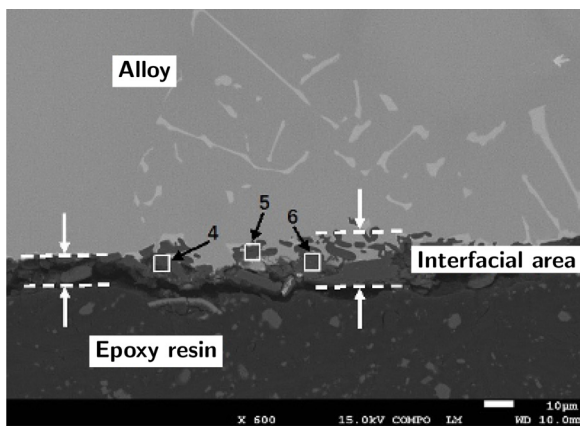


Fig. 13. Interfacial area image of fused alumina face coat with 5 wt% Cr_2O_3 (reprinted with permission from Ref. [60]).

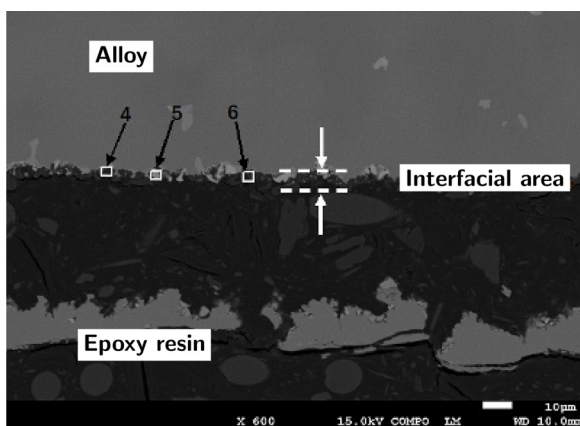


Fig. 14. Interfacial area image of fused alumina face coat with 5 wt% h-BN (reprinted with permission from Ref. [60]).

reactions. This was supported by multiple studies which used modified alumina face coats to mitigate interfacial reactions. An initial study showed that by including an additive ceramic powder composed of hexagonal boron nitride (h-BN) and calcined kaolin in quantities of 5 wt %, a noticeable reduction in wettability of the alloy on the face coat can be achieved [63]. In a subsequent study, a fused alumina face coat with varying h-BN additions was compared to alumina face coats with varying Cr_2O_3 contents and the resulting reaction layers can be seen in Figs. 13 and 14. It was shown that the h-BN additions were successful at increasing the wetting angle and thus decreasing melt permeation into the face coat, while the Cr_2O_3 showed no potential for mitigating interfacial reactions [60]. Another method for barrier application stems from the deposition of a thin aluminum coating on the surface of the mold, which makes the mold electrically conductive. This surface can then be subject to electrostatic powder coating while the metallic layer is simultaneously consumed in a reaction to alumina, becoming part of the reaction-inhibiting barrier coating itself [22].

3.2. Rapid prototyping and additive manufacturing

To overcome common limitations of traditional shell-forming

techniques, including lack of control over thickness and preferential chemistry, recent research has utilized rapid prototyping and additive manufacturing (AM) to yield more authority over the structure of the shell. As previously discussed in the review, the edges of ceramic molds act as potential sites for mechanical failure as a result of stress concentrations and reduced shell thickness [33]. Traditional dipping techniques fall short of counteracting this effect, sacrificing other necessary properties such as permeability in order to manufacture sufficient strength to avoid crack propagation [35]. Through AM techniques, manufacturing flexibility is significantly increased to allow for the formation of composite designs to generate preferentially located zones of differing chemistry, thickness, and/or various mechanical and thermal properties.

Control can be extended beyond simple dimensional alterations and into structural design as well by utilizing stereolithography to form layered components. Stereolithography is an AM technique which utilizes photochemical processes to sequentially build up layer by layer. In this case, each individual coat can be designed with regard to the desired function of the part to form a functionally graded component [64]. The process has several potential benefits when compared to slurry-based counterparts because it allows for manipulation of layered properties to develop a more viable shell. It has been shown that an AM process can be utilized to formulate an outer core body layer comprised of a more expensive, highly non-reactive yttria-based powder while using a cheaper, more leachable ceramic for the body of the core. This allows for the utilization of the non-reactive nature of yttria-based ceramics with the superalloy melt while mitigating the negative effects of its limitations, discussed in the yttria subsection (4.4). Also introduced were sub-layers between the outer core layer and the core body to alleviate thermally-induced stresses from differences in expansion coefficients and to improve the sintering behavior [65]. Additive manufacturing can be taken even a step further to not only influence the composition and structural control of the mold but to incorporate geometrical alterations as well. For example, AM can be utilized to incorporate leachant-enhancing voids and channels to facilitate the removal of thicker, less leachable areas of the core. This relationship between porosity and leachability is one that has been well established, both in relation to ceramic core processing as well as other applications, [66,67] and can be easily exploited through the use of AM techniques. An additional capability of additive manufacturing is to form wax patterns directly, rather than through injection molding. Several researchers have noted the benefits of AM in this application, as it reduces the rather significant tooling time and cost that comes with the standard injection molding process and pattern assembly [68,69].

3.3. Gel-casting

Gel-casting is a form of manufacturing ceramic cores often used in conjunction with additive manufacturing techniques. It is a near-net shape process by which ceramic powders are placed in an organic monomer solution before being poured into a mold. Gel-casting allows the mixture to polymerize into a strong, cross-linked gel with high strength and a relatively short development cycle [70]. A gel-casting process was successfully developed for the low-cost production of alumina-based ceramic cores by utilizing a freeze-drying process to minimize shrinkage and suppress the formation of cracks, as illustrated in Figs. 15 and 16 [71]. Further control over shrinkage can be accomplished by way of magnesium oxide powder additions to levels below 0.5%, which through expansive formation of MgAl_2O_4 is able to

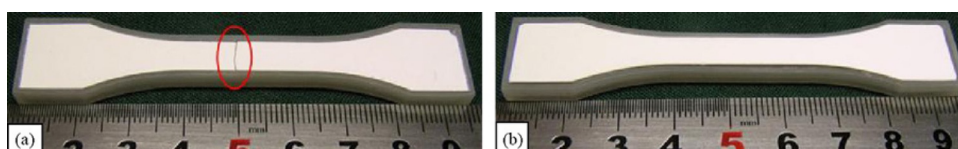


Fig. 15. (a) Crack resulting from air drying and (b) suppression of crack formation due to air drying process (reprinted with permission from Ref. [71]).

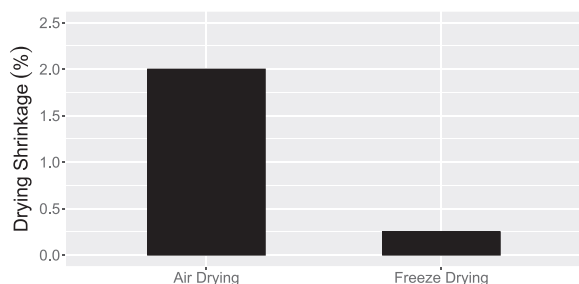


Fig. 16. Comparison of air-drying shrinkage and freeze-drying shrinkage showing that freeze drying resulted in a significantly lower drying shrinkage (redrawn with permission from Ref. [71]).

counterbalance the natural sintering shrinkage of the core [71,72].

As previously referenced, gel-casting can be used with complementary techniques to enhance various processing parameters. In one investigation, AM was used with gel-casting to rapidly develop complex resin mold prototypes to replace standard metal dies. These molds, in addition to lower costs and lead times, offer high forming accuracy, good rigidity, and improved surface quality [71]. A ceramic core was similarly developed through gel-casting to be used for the casting of aluminum, magnesium, and titanium alloys. For this method, a calcia-based slurry was utilized along with a water-soluble epoxy resin to form a homogeneous green body with a green density of 58.5% and a high flexural strength of 29.5 MPa. Additionally, the water-solubility of the core helped to overcome leachability limitations to facilitate easy removal of the core after casting [73]. Despite these promising properties, the relatively high sintering shrinkage of over 11% represents significant potential for cracking, a problem that faces many gel-casting processes. Furthermore, no existing evidence was found to show that this process can be applied to nickel-based superalloys.

Another critical processing consideration, as referenced several times previously, is the permeability of the ceramic mold which allows for the displacement of gas through the shell. To augment the permeability of fired ceramic molds, many processes utilize pore forming agents (PFAs) in ceramic slurries, which burn out during firing to leave behind voids and increase shell permeability. As a result of the aforementioned difficulties commonly associated with the transition to fiber PFAs, several recent studies reverted back to a close derivative of traditional pore-forming techniques in a process known as needle coking during which a crystalline petroleum coke is utilized as a filler in the ceramic slurry. Needle coke in particular is extremely desirable due to its high strength, low expansion coefficient, good resistance to thermal shock, and low cost [74]. Needle coke additives increased overall shell thickness by 30% and edge thickness by 60% compared to traditional fused silica molds without the need for additional coats, which act to reduce permeability and increase production times. Moreover, the shells containing petroleum-induced pores exhibited a larger green strength and comparable hot strength when compared to the fused silica system, which indicates a desirable retention of strength even in the presence of increased porosity as seen in Figs. 17–19 [74,75].

4. Ceramic materials

As discussed, the ceramic material used for the investment casting mold significantly influences the viability of the casting system and process. Included at the forefront of these considerations are aspects such as reactivity, leachability, mechanical properties, thermo-mechanical properties, and processability. Ceramic oxides have proven to be the most successful ceramics for superalloy casting as they tend to better avoid reactions with the melt. The major ceramics utilized in ceramic mold designs—and those that will be discussed for the purposes of this review—are silica, alumina, zircon, and yttria-based materials. The historical performance of these ceramics as they relate to

the aforementioned integral properties is examined below.

4.1. Silica

Silica-based components, formed from fused silica (SiO_2), are some of the most popular ceramics for the casting of superalloy components. As a polymorph, the properties of silica can vary significantly based upon its phase. The primary phases of silica that will be discussed below are fused silica, which is its amorphous form, and cristobalite, which is a high-temperature mineral polymorph. In its amorphous state, it offers several benefits in high-temperature environments, including an exceedingly low thermal expansion coefficient of $0.6 \times 10^{-6} \text{ K}^{-1}$, which results in a high thermal shock resistance. Fused silica also has good leachability properties and is able to be removed through the use of NaOH and KOH, aqueous solutions which avoid harming the cast alloy itself [24]. One of the most influential characteristics of fused silica however is the controllable nature of its mechanical and thermal properties. Standard fused silica can soften, which makes it susceptible to distortion due to forces during sintering, including creep. This problem can be solved by improving the strength of the mold, which largely is dependent on two factors: apparent porosity and cristobalite transformation [24]. Cristobalite is a mineral polymorph of silica which forms on the surface of fused silica grains during sintering from the reconstructive transition of silica at high temperatures [76]. This transformation dominates the sintered behavior of fused silica-based ceramic materials at elevated temperatures, as in casting applications, by providing a strength increase to the core. Initial transformation to the β -cristobalite phase has been shown to increase the strength and bulk density of a fused silica mold, as the flexural strength of samples sintered at 1300 °C (11.4 MPa) displayed drastic improvement from samples sintered at 1200 °C (1.9 MPa) as shown in Fig. 20 [24].

Several researchers note however that this β -cristobalite transformation is only beneficial to the performance of fused silica molds in moderation, indicating that silica-based molds applied to superalloy casting should ideally contain just 10–20% cristobalite [76,77]. At sintering temperatures of 1500 °C, despite a relative density increase and almost 78% cristobalite transformation, the flexural strength decreased from over 11 MPa for a sintering temperature of 1350 °C to 4.6 MPa [24]. This excess cristobalite is problematic during cooling of the mold when, at 220 °C, the cubic β -cristobalite undergoes a conversion to tetragonal α -cristobalite as a result of stereochemically unfavorable chemical features such as the 180° Si–O–Si bond angle and shorter bond length [78], which is accompanied by a 4% volume contraction. This contraction can generate microcracks in the ceramic, diminishing the flexural strength of the silica at room temperature [24].

Furthermore, the high melting temperature, low ductility below 500 °C, and compromised strength at high-temperature of many Ni-based alloys can make them more susceptible to cracking, particularly in NiAl alloys [79,80]. It has been shown that by adding zircon to the silica-based ceramic, a material with greater high-temperature strength in comparison to its fused silica counterpart, it is possible to both reduce the presence of cristobalite and increase the modulus of rupture (MOR) of the ceramic (Fig. 21) while simultaneously increasing open porosity. This occurs as a result of increased zircon content, which is accompanied by a reduction in fused silica. Given that cristobalite crystallization occurs on the surface of silica particles, it is understandable that a reduction in fused silica would cause a similar reduction in cristobalite content as seen in Fig. 22 [81,82].

Furthermore, fused silica molds have, relative to many of their ceramic counterparts, shown a tendency to react with some of the more chemically active alloying elements found in nickel-based superalloys such as Al, Hf, Ti, Zr, Cr, and C. These interactions between the mold and alloy melt reduce the concentration of the active elements in the melt and produce undesired reaction layers at the surface. The reaction kinetics are exacerbated at temperatures exceeding 1500 °C meaning that in conjunction with predominant cristobalite transformation at

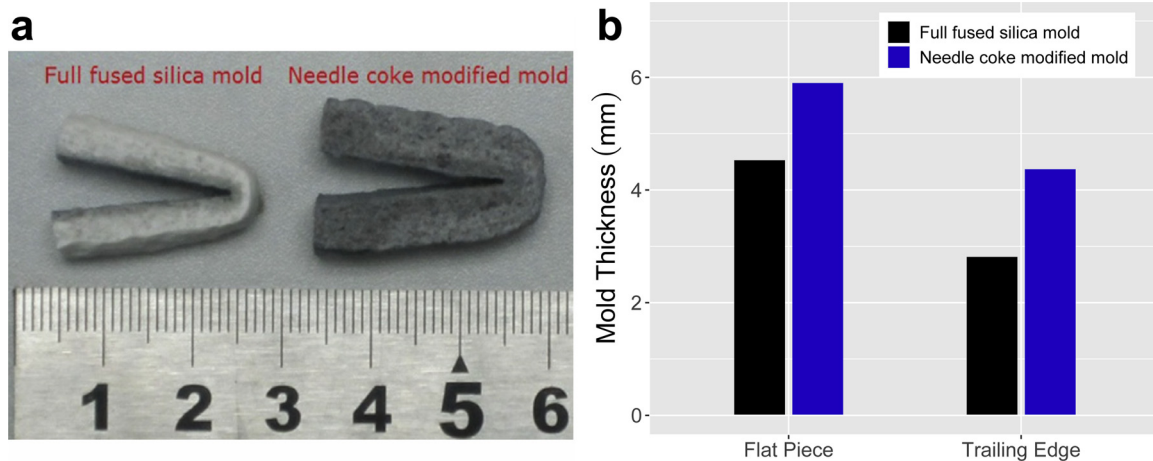


Fig. 17. Mold thickness comparison of a flat sample and trailing edge sample of fused silica mold vs. a needle coke modified mold with (a) a side-by-side image of samples prepared with each composition and (b) a quantitative comparison of flat pieces and trailing edges (redrawn with permission from Ref. [74]).

elevated temperatures, it severely limits the performance of silica in high-temperature casting environments [83,84].

4.2. Alumina

Alumina (Al_2O_3) exhibits several beneficial characteristics that make it a desirable ceramic mold material for superalloy processing. One of these benefits of alumina is that it is able to be removed through the use of aqueous solutions such as aqueous HF and KOH, similar to silica molds, which allows the ceramic core to be removed from the cast part while mitigating damage to the alloy. Several studies, however, indicate that the removal of alumina cores by chemical leaching can be rather sluggish compared to other widely used ceramic core materials. Silica additives have proven to be beneficial in improving this leachability while concurrently improving porosity and creep resistance, though with some detriment to bending strength [66,85]. Furthermore, alumina has desirable high-temperature behavior such as its high thermal conductivity and thermal expansion identical to that of corundum casting shells when used as a core material, which is helpful for dimensional accuracy of the cast part [66]. Lastly, the properties of an alumina-based ceramic can be easily controlled through kyanite addition, a silica-aluminate which induces favorable mechanical and creep properties (Fig. 23) as well as low sintering shrinkage (Fig. 24) when utilized as an additive in alumina molds. An investigation into the

directional solidification of a single crystal nickel superalloy blade attributes these properties to in situ synthesis of mullite by way of kyanite decomposition [86].

Alumina however does suffer from some properties that limit its capabilities as a single material for ceramic investment casting shells and cores. Several researchers critically note that alumina-based molds experience substantial interfacial reactions with alloying elements in nickel superalloys such as Cr, Hf, and Al [60,87,88]. The reactions specifically form so called sand-burning defects, which result from chemical adhesion of “sand” onto the surface of the cast component and reduce dimensional accuracy and increasing processing cost of the component [89]. Furthermore, it has been shown that some alumina molds suffer from deficient green strength, although some studies demonstrate that this can be heavily influenced by the binder used in the ceramic slurry. Utilizing more efficient binders such as silica sol or polyvinyl alcohol, the mechanical properties of the green body can be significantly enhanced as shown for silica sol in Fig. 25 [55,90,91].

Highly pure alumina molds also tend to induce hot tearing of the solidifying alloy, which manifests as longitudinal grain boundary defects that occur during the final stages of solidification. This is primarily because when the volume fraction of the solid phase is high, the feeding of liquid metal which would normally compensate for volume contraction can be inhibited by barriers formed by the already solidified alloy regions. Because of this impediment, the remaining interdendritic

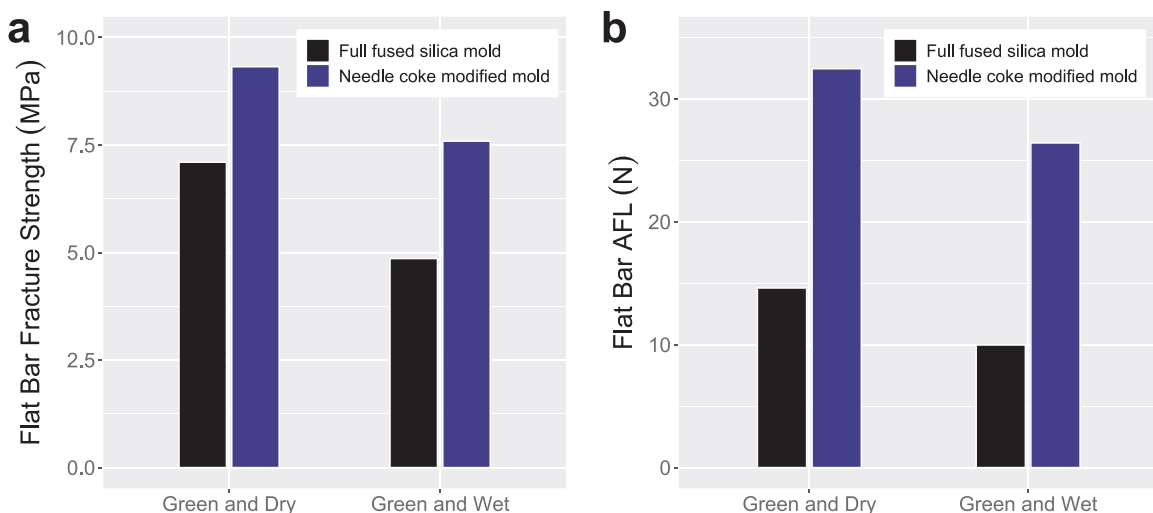


Fig. 18. Comparison of strength and load capacity of green mold samples: (a) MOR and (b) AFL (redrawn with permission from Ref. [74]).

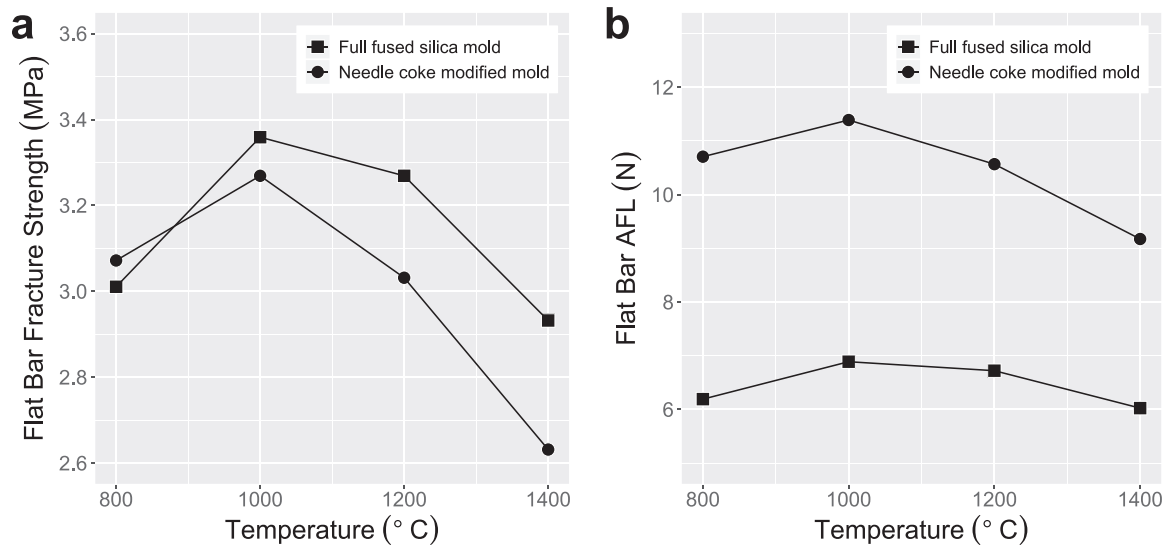


Fig. 19. Comparison of strength and load capacity of hot mold samples: (a) MOR and (b) AFL (redrawn with permission from Ref. [74]).

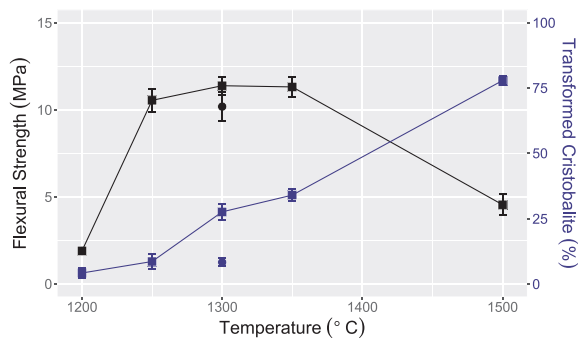


Fig. 20. Flexural strength and transformed amount of cristobalite of test bar sintered as a function of different sintering temperatures. Square and circle samples held for 2 and 0.5 h, respectively (redrawn with permission from Ref. [24]).

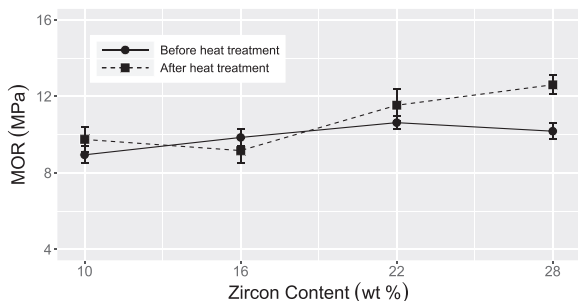


Fig. 21. MOR results of the ceramic cores with various zircon contents before and after the heat treatment (redrawn with permission from Ref. [81]).

liquid has insufficient resistance to stresses and strain which can form due to phase transformation and subsequent thermal contraction during cooling [92–95]. In the case of alumina, the pure ceramic can become excessively strong during sintering, which may prevent the mold from yielding during alloy contraction. This induces significant residual stresses in the alloy and increases susceptibility to hot tear formation [79,92]. The high strength of alumina can be utilized, however, by using alumina powder as a partial filler in a ceramic slurry of another ceramic base-material to augment mechanical properties. For example, it was recently reported that by using a mixture of alumina with zircon as opposed to pure zircon, it is possible to improve both the flexural strength and refractoriness [96].

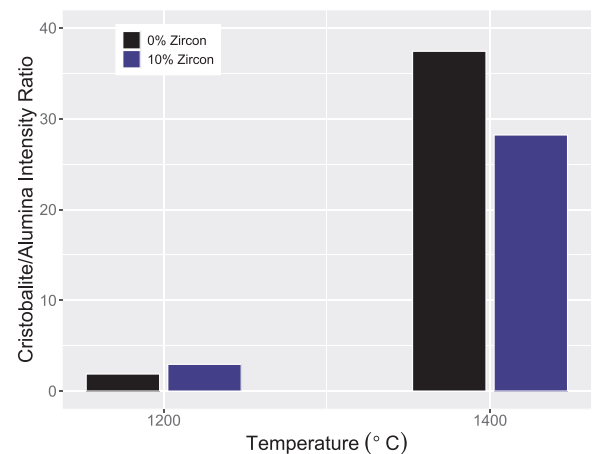


Fig. 22. 100% peak intensity ratio of cristobalite to alumina for the sintered samples at 1220 °C for 6 h with and without zircon before and after heat treatment at 1400 °C for 1 h (redrawn with permission from Ref. [81]).

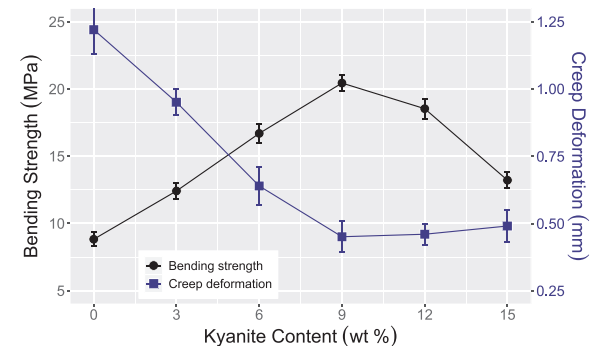


Fig. 23. Effect of the kyanite content on the bending strength and creep deformation of alumina-based molds at 1550 °C. Both strength and creep deformation improve linearly from 0 to 9 wt% kyanite. Property deterioration at temperatures above 1550 °C result from reduction of density due to the volume expansion accompanying kyanite decomposition to mullite (redrawn with permission from Ref. [86]).

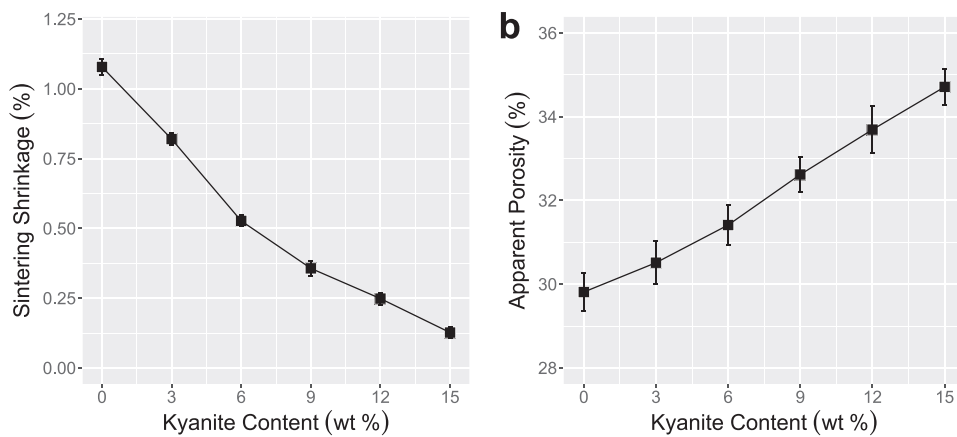


Fig. 24. Effect of the kyanite content on the (a) sintering shrinkage and (b) apparent porosity of alumina-based molds. Sintering shrinkage reduces and apparent porosity increases linearly with increase from 0 to 15 wt% kyanite due to significant volume expansion accompanying kyanite transformation (redrawn with permission from Ref. [86]).

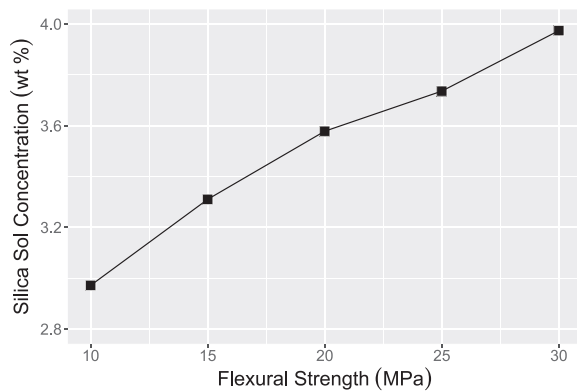


Fig. 25. Flexural strength of the green body vs. silica sol concentration in the slurry. Solid volume loading is fixed to be 50 vol%. Linear increase in flexural strength from 2.97 to 3.98 MPa results from an increase in silica sol binder concentration from 10% to 30% (redrawn with permission from Ref. [90]).

4.3. Zircon

Zircon (ZrSiO_4), otherwise known as zirconium silicate, represents a promising ceramic mold material both as the primary base and as an additive to other oxide-based slurries. When used as a principal slurry material it is known as zircon flour, which is a fine mineral powder made from zircon sand. This ceramic material is popular in the investment casting industry for several reasons, particularly its desirable thermal properties. Zircon has a low thermal expansion coefficient of approximately $4.1 \times 10^{-6} \text{ K}^{-1}$ below 1400°C and no phase transformations up to 1675°C [82,97]. These properties aid with stability to prevent both dimensional defects and residual stresses in the casting that result from thermal displacement of the mold during casting. Furthermore, zircon exhibits significant high-temperature chemical inertness which allows it to be utilized in the extreme environments required during superalloy processing without suffering from significant interfacial reactions with the alloy melt [98]. In conjunction with its valuable thermal and chemical properties, zircon offers desirable mechanical properties as well, such as improved strength over fused silica molds which often suffer from deficient green and fired flexural strength. Moreover, a primary slurry made of 100% zircon has been shown to yield casting with a uniform microstructure with desirable surface morphology and directional solidification when compared with alumina and silica containing samples (Figs. 26,28) [99].

Due to the notably higher cost of zircon compared to fused silica and alumina, zircon is used as a filler or in conjunction with other additives rather than as the sole base material [30] in order to utilize the beneficial properties of zirconium silicate while minimizing expense. As previously discussed, zircon additions to a fused silica slurry can help

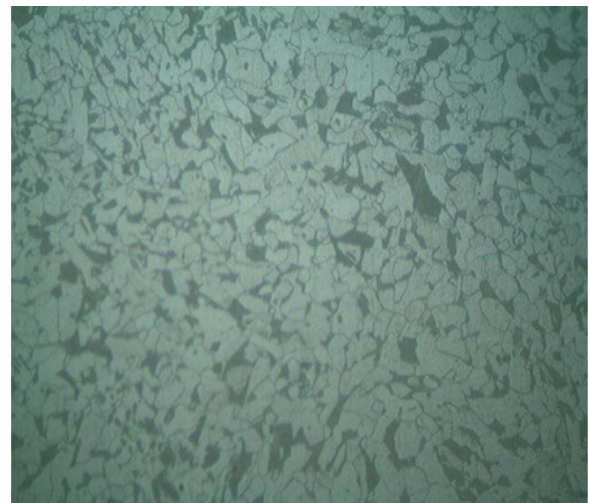


Fig. 26. Micrograph of sample A containing 100% zircon (400 \times) (reprinted with permission from Ref. [99]).



Fig. 27. Micrograph of sample B containing 50% zircon and 50% alumina (400 \times) (reprinted with permission from Ref. [99]).

improve both the flexural strength and creep resistance of the mold [81,82]. By adding zircon to alumina, an improved surface finish can be accomplished without sacrificing mechanical properties [99]. Relative to many of its oxide counterparts, however, zircon does suffer from a relatively poor leachability [81,83]. As such, in applications where



Fig. 28. Micrograph of sample C containing 70% zircon and 30% silica (400×) (reprinted with permission from Ref. [99]).

leachability is the primary concern relative to mechanical performance, it may be beneficial to utilize a high-silica ceramic over prioritizing zircon content [100] though this circumstance is unlikely in the casting of superalloys.

4.4. Yttria

Yttria (Y_2O_3) is a lesser used rare earth oxide (REO) relative to the aforementioned ceramic oxides, but has significant potential for the high-temperature investment casting of superalloys. This is in large part because yttria displays one of the lowest Gibbs free energy per mole of oxygen of any known oxide material, which is beneficial for minimizing chemical reactions between the mold and the metal particularly with respect to both nickel superalloys and high-performance molten titanium [101,102]. It was shown that an yttria core was able to result in better retention of reactive elements in nickel superalloy CMSX-4, more successfully mitigating reaction layers by several-fold when compared to alumina and silica-based cores [101]. Despite its desirable chemical properties, however, yttria is rarely found in commercial use. This is predominantly due to its material cost, which is appreciably higher even than that of zircon. This cost is further exacerbated by its high sintering temperature of over 1400 °C [103], which increases processing and production cost of yttria molds. Yttria also faces another inherent problem, with rapid hydration of yttria particles causing an yttria-based slurry to gelate soon after preparation [104]. It has been shown, however, that the shelf life of a yttria-based slurry can be significantly extended by introducing a source of hydroxyl ions into the slurry to reduce hydration kinetics, such as NaOH (Table 1) [105]. Likewise, an ammonium zirconium carbonate binder in conjunction with fluorine-containing dopant has been shown to achieve a similar delay in gelation behavior [106].

Although the addition of additives providing hydroxyl ions was a

large step for the commercial utilization of yttria-based slurries, yttria remains extremely cost prohibitive as a single material for mold applications. To an extent, both of the cost and hydration issue can be mitigated through additions such as zirconia which exhibits both a lower susceptibility to hydration and a lower cost [104]. Given the desirable corrosion resistant nature of yttria as it relates to the casting of alloys containing rare earth metal active elements, additional research is being applied to yttria-based ceramic molds to further utilize the oxide in the casting of superalloys and other high performance metals.

4.5. Material overview

As a result of these thermal, chemical, and mechanical characteristics specific to each individual ceramic option, the viability of these materials for mold applications can be heavily influenced by the requirements of the system and the nature of the cast alloy. One of these major determinants in the choice of material is the processing temperature. For more thermally demanding applications, materials with lower thermal expansion and improved thermal shock resistance, such as silica and zircon, are strongly preferred. These thermal characteristics also mitigate mechanical stresses placed on the alloy during solidification and reduce the risk of defect formation. Additionally, less reactive materials are generally considered for these applications as the increased temperatures tend to exacerbate interface reactions [107]. As such, more susceptible materials, such as fused silica, tend to generate prominent reaction layers on the surface of the alloys during casting. Furthermore, silica suffers from significant phase transformations at temperatures below common casting temperatures of superalloys, as discussed in Section 4.1. These transformations are often accompanied by notable changes in volume and thermal expansion [108], resulting in aforementioned dimensional and structural defects [24]. Options such as zircon fare far better at these elevated temperatures, with lower thermal expansion and no phase transformations below 1700 °C [82].

Similarly, another factor in determining the best mold material is the mechanical strength of the cast alloy. As previously discussed, the relative strengths of the ceramic mold and alloy can play a large role in the uniformity of a component as well as mitigating defect formation during casting. Excessively low high-temperature strength of the mold has a propensity to result in premature deformation or failure of the core during alloy solidification, leading to dimensional defects in the component. Conversely, an excessively high core strength, as can be found for example when using pure alumina, can cause cracking in the alloy as residual stresses are induced during cooling while the component is weak [92]. Because of this, it is important to select a mold material which has mechanical properties that are well suited to the mechanical stresses that will be induced during casting to provide sufficient strength during solidification but allow for collapsibility where necessary to avoid excessive stresses due to alloy shrinkage.

5. Testing and characterization

There are several critical properties of ceramic molds that determine

Table 1
Gelation behavior of yttria slurry as a function of NaOH content (redrawn with permission from Ref. [105]).

Sample	Mass NaOH (g)/228 mL H ₂ O	SiO ₂ /Na ₂ O (equivalent) dry mass ratio	Observations
1	None	42.8/1	Gelled within 5 days
2	0.19	35/1	After six days had settled and could not be readily redispersed. However, liquid on top was not gelled
3	0.36	30/1	Same as sample 2
4	0.61	25/1	After 6 days had settled, but could not be readily redispersed
5	0.97	20/1	Same as sample 4
6	2.79	10/1	Same as sample 4
7	6.43	5/1	Same as sample 4

Table 2
Summary of useful characterization standards for relevant properties.

Measurable	Characterization technique	Relevant standard(s)	Description of ASTM standard
Flexural strength	3-Point bend test	ASTM C1211, ISO 17565	Determination of the flexural strength of advanced ceramics at elevated temperatures
Surface morphology/microstructure	Scanning electron microscopy (SEM)	ASTM STP827, ISO 13383-1	Guide for investigating fractography of ceramic and metal failures
Porosity	Mercury intrusion porosimetry	ASTM UOP578, ISO 5016	Determination of pore size distribution and pore area of materials by mercury intrusion
Reaction product/composition	Electron probe micro-analysis	ASTM E1508, ISO 19463	Guide for quantification of elemental composition of phases in a microstructure
Thermal expansion	Thermal dilatometry	ASTM C1470, ISO 17139	Guide for testing the thermal properties of advanced ceramics
Thermal diffusivity	Laser flash method	ASTM C1470, ISO 8894-2	Guide for testing the thermal properties of advanced ceramics
Linear shrinkage	Dimensional measurement	ASTM C326, DIN EN 725-11	Standard test method for drying and firing shrinkage of ceramic whiteware bodies

their viability for the investment casting of any alloy. As it pertains to the casting of nickel-based superalloys, many of these property requirements are intensified as a result of the higher thermal, chemical, and mechanical demands that the mold is subjected to during the casting process. For the purposes of this review, the main properties that have been highlighted as critical to the processing and application of a ceramic mold are both green and fired flexural strength, chemical inertness, porosity, microstructure, thermal conductivity, and thermal expansion. As such, it is valuable to examine characterization methods of these properties to be able to determine the viability of various material options in investment casting of nickel superalloys. A summary of predominant characterization techniques is shown in Table 2 and is followed by a more in depth review of material testing for each individual property.

5.1. Mechanical properties

Mechanical properties at both room temperature and elevated temperatures play a large role in the dimensional accuracy and stress-handling capabilities of a mold material. In the case of investment casting this comes primarily in the form of flexural strength, as the ceramic mold is more susceptible to transverse stresses during casting of solidifying alloys, as well as secondary properties such as Young's modulus and fracture toughness. These stresses, which induce crack propagation in the mold, can lead to dimensional distortion or fracture in the mold to compromise the cast component. Flexural strength is most commonly tested in bending through the use of 3-point or 4-point bend tests. An example of this comes in a recent paper on a refractory fused silica based ceramic mold, where 8 mm × 8 mm × 83 mm samples are fabricated to be subjected to a 3-point bending test to determine the flexural strength of various samples sintered at different temperatures. In this particular case, the effect of the cristobalite formation on the strength of the samples was determined [24]. Similarly, the use of 3-point bend tests aided in determining the flexural strength of a gel-cast, calcia-based ceramic core in its green state to investigate the effect of the gel-casting method on the properties of a calcia mold [73].

There are, however, several challenges associated with characterizing mechanical strength at high temperatures relevant to superalloy investment casting. For these properties, in addition to requiring a substantial amount of energy, the process of testing samples at elevated temperatures can be time consuming due to the limited number of samples that can be analyzed at a time [109]. Additionally, when taking measurements, it is vital that the testing chamber is homogeneously heated so that temperature of the material sample is uniform. Uneven heating of the test sample can lead to inconsistent thermal expansion of the material and result in inaccurate or inconsistent measurements as well as stress development [109]. This can be especially relevant for complex patterns such as those commonly found in investment casting molds where uniform heating is made more difficult at acute geometries. Features such as corners or leading edges have lower local strength, making them particularly susceptible to defect formation. [32]. Another complication of testing at elevated temperatures is the possibility of creep or slow crack growth interfering with results. This phenomena is particularly pertinent during a 3-point or 4-point bend test of an investment casting mold, given the susceptibility of ceramics to creep under tension [110,111]. Furthermore, the presence of various interfaces in the mold due to functional grading can generate residual stresses during cooling as a result of mismatch of thermal expansion coefficients. This often leads to the nucleation and propagation of interfacial cracks which compromise the mechanical strength of the mold and lead to delamination of its layered structure [112].

5.2. Microstructure

Microstructural characteristics of any material, including ceramic molds, are one of the largest driving factors of the properties and performance of the finished component. In most cases, the microstructure of a sample can be examined through scanning electron microscopy (SEM) as well as other microscopy techniques to reveal compositional and topographical information about a material. For example, the SEM image presented in Fig. 29 shows the cross-section of a CaZrO₃ mold resulting from the application of five sequential layers with indicated grain-sizes, yielding an apparent porosity and median pore diameter of

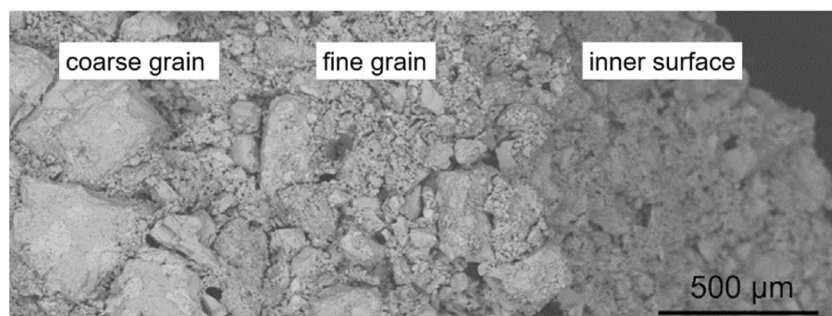


Fig. 29. Cross section SEM image of a CaZrO₃ investment casting mold with 5 coats, comprised of 2 front coats of S_{0.5} followed by 3 coarse-grained secondary coats of S₁. On the right there is the inner surface with a fine-grained structure, on the left the coarser grains of the secondary coats are clearly visible (reprinted with permission from Ref. [116]).

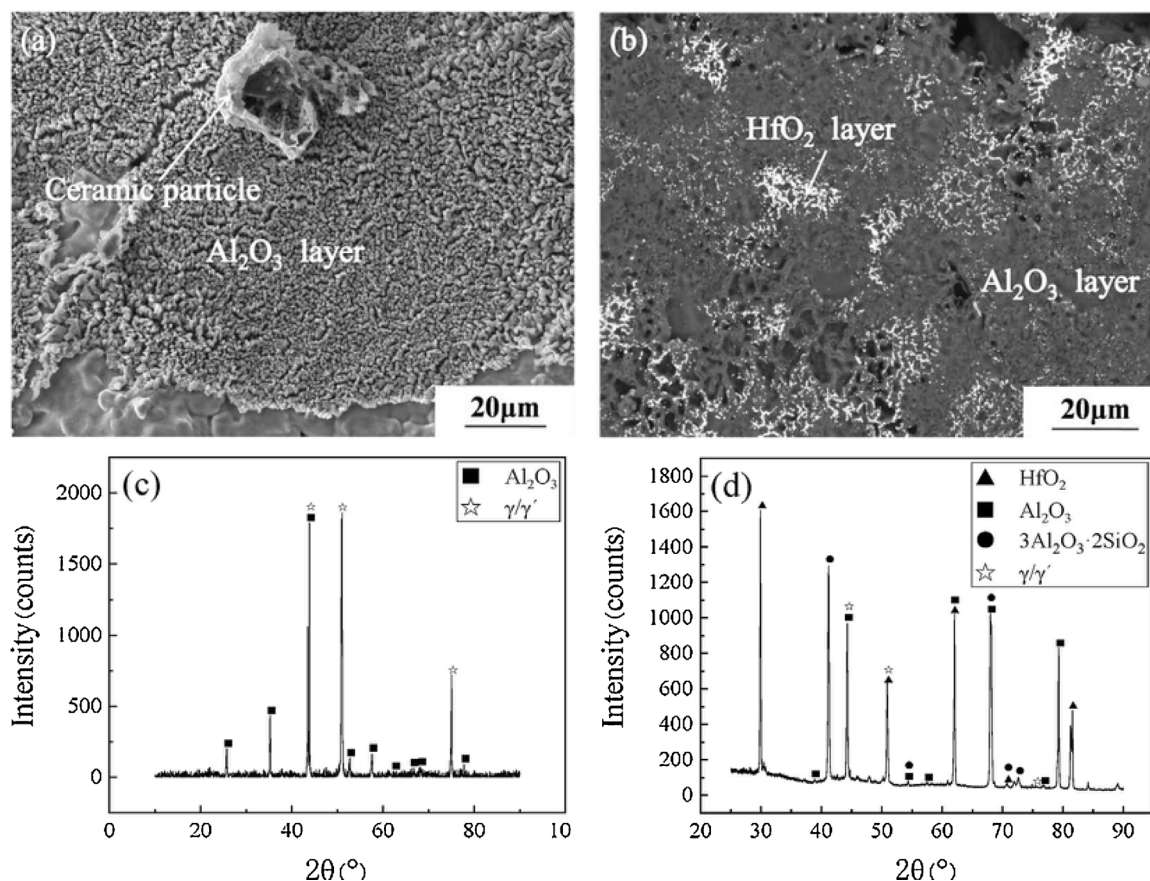


Fig. 30. SEM images and XRD patterns presenting the interface reaction of a nickel-based superalloy containing 0.008 wt% yttrium with a alumina ceramic surface using the sessile drop method: (a) microstructure of the alloy bottom, (b) microstructure of the ceramic surface, (c) XRD pattern at the alloy bottom, (d) XRD pattern on the ceramic surface (reprinted with permission from Ref. [115]).

approximately 22.6% and 19.1 μm respectively. The resulting grain size distribution can clearly be seen in the graded cross-section, with finer grains at the inner surface and a more coarsened-grained microstructure at the secondary coats. Furthermore, to investigate the bonding of the sequential layers of graded refractories including investment casting shell molds, X-ray computed tomography has been applied [113,114].

In a separate investigation, SEM was utilized to examine fracture micrographs of both the green and sintered core body and determine the homogeneity of samples. It was found that both the green and sintered bodies displayed micropores in the midst of a uniform microstructure, which may be beneficial to prevent cracking and promote permeability of the mold [73]. More recently, SEM was used in conjunction with electron probe micro-analysis (EPMA) to investigate the reaction products and elemental compositions which resulted as a function of yttria content in a silica mold when casting a nickel-based single-crystal superalloy. Subsequently, using X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS), phases of these products were identified and analyzed [115] as shown in Fig. 30. Using these techniques in coordination with one another, the reaction products at increasing yttria contents were compared to determine both the mechanism and product of the interface reactivity. This research provides good insight as to the effectiveness of some of the different techniques in examining various microstructural characteristics and how they can be used in tandem to develop a complete microstructural understanding. Other studies used these techniques in a similar manner, such as using XRD to measure phase transformations in a silica microstructure to investigate cristobalite transformation as a function of temperature and time [100].

5.3. Porosity

Porosity, which is directly related to permeability, is critical to the function of the mold as it affects transport of heat and gas through the ceramic. Open porosity and pore size distribution can largely be determined through two separate methods, those being the Archimedes method and mercury porosimetry. A study on calcium zirconate molds utilized each of these methods, first using the Archimedes principle to deduce the apparent porosity in the ceramic material by using water as the immersion medium. Mercury intrusion porosimetry was subsequently used to determine the pore size distribution within the calcium zirconate mold, which is useful to ascertain the uniformity of the pore structure (Fig. 31) [116].

These porosity measurements are critical as they are closely related to the permeability of the shell and its ability to release gas through the shell wall during pouring. Furthermore, when applied to a ceramic core, porosity is a good indicator of leachability, with open porosity providing channels for leachant penetration. Porosity also inversely affects relative density and, typically, has an inverse relationship both with mechanical strength [71,117] and Young's modulus [118,119]. As such, it can often be used to estimate mechanical susceptibility. Of critical importance in these measurements is open porosity as opposed to total porosity, which is a more accurate indicator of permeability and leachability. Closed porosity, though it may affect the relative density and mechanical properties of a component, does not significantly aid in transport through the mold.

5.4. Chemical reactivity

In the case of high corrosion resistance of the ceramic molds to the

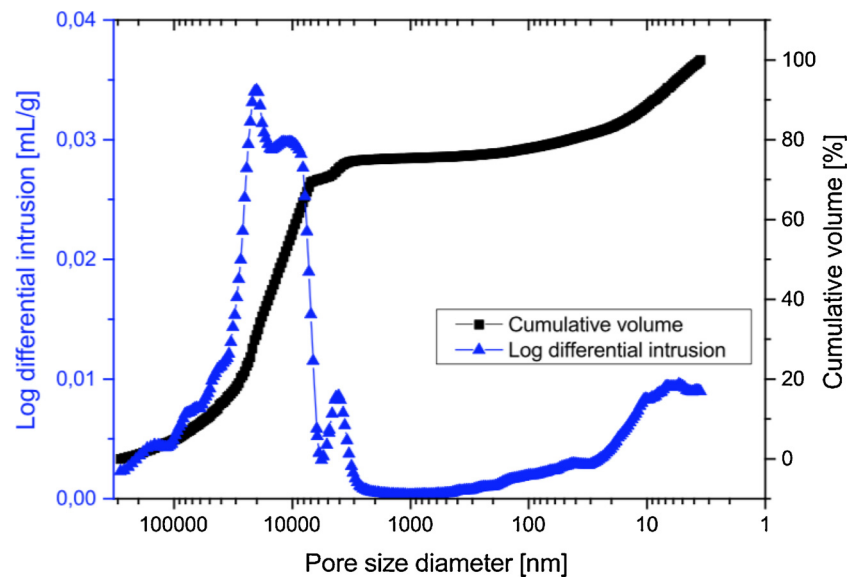


Fig. 31. Pore size distribution of a coarse-grained investment casting mold with 5 coats (reprinted with permission from Ref. [116]).

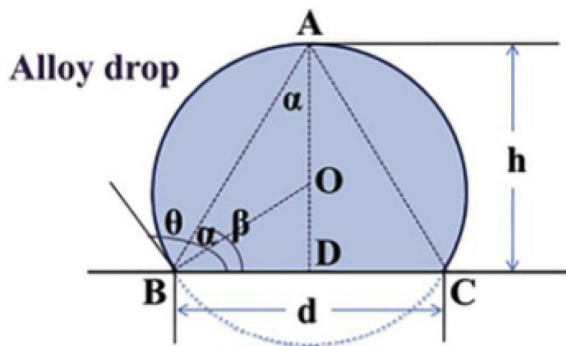


Fig. 32. Schematic representation of a wettability of an alloy drop on a substrate as a function of its height (h) and diameter (d) (reprinted with permission from Ref. [115]).

superalloy melt, it is difficult to directly examine the chemical reaction mechanisms that take place at the mold-metal interface. As a result of this, details of the exact reactions that occur in the system still remain largely unestablished. In order to analyze the reactions that occur at the ceramic/metal interface, however, it is possible to investigate the reaction layer that forms at the surface of the mold. For instance, in an investigation using a sessile drop test (Fig. 32), a Ni-based superalloy was placed on a ceramic substrate and heated at 1550 °C under vacuum atmosphere to induce chemical reactions at varying yttria contents in the alloy [115].

Sessile drop experiments are effective because they are able to simultaneously investigate reactivity as well as wettability, which are closely related [120]. Increased wettability between the melt and the mold allows the molten alloy to infiltrate capillaries of a mold face coat and aggravate interfacial reactions [60]. The Young-Dupré equation, which is used to relate the contact angle (θ) of a liquid droplet on a substrate to the solid surface free energy (γ_{sv}), solid/liquid interfacial free energy (γ_{sl}), and liquid surface free energy (γ_{lv}), is given below:

$$\cos \theta = \frac{\gamma_{sv} - \gamma_{sl}}{\gamma_{lv}} \quad (1)$$

Scanning electron microscopy (SEM) (Fig. 30a and b) is then often used in conjunction with energy dispersive spectroscopy (EDS) to examine surface morphologies at the reaction interface. In addition, electron probe micro-analysis (EPMA) was conducted for compositional

analysis with X-ray diffraction (XRD) (Fig. 30c and d) utilized to determine present phases. Finally, reaction products can be determined at the surface of reaction products by way of X-ray photoelectron spectroscopy (XPS). Using these methods, it was found that the reaction products that occurred between lower and higher yttria content levels in the alloy changed from Al_2O_3 and HfO_2 to various Y-Al-O compounds, with the thickness of the reaction layers increasing rather significantly with higher yttria content [115]. Other researchers have also used sessile drop tests, for instance to study the interaction between a yttria-zirconia blended face coat and a high-performance titanium alloy. Similarly, SEM was again used to examine the resulting interfacial microstructures [104].

5.5. Thermal properties

One of the most important thermomechanical properties of a ceramic shell or core is its thermal shock resistance, which is indicative of its ability to withstand rapid changes in temperature. Thermal shock resistance is a function of several various properties, with the most influential properties being thermal expansion, thermal conductivity, tensile strength, work of fracture, Young's modulus, thickness, shape and especially microstructure [117,121,122]. Each property plays a large role in a material's ability to avoid instable crack propagation in reaction to extreme thermal stress, and it is therefore essential to accurately characterize them for high-temperature applications. One study utilized a thermal dilatometer to determine linear thermal expansion of alumina-based molds with varying kyanite content as a function of temperature. This allowed the group to use the dilatometry data to not only develop a visual model of expansion vs. temperature but also determine the governing basis of the linear shrinkage [71]. Alternatively, other researchers were also able to test dimensional fluctuation of samples by way of simple dimensional measurements to determine linear and sintered shrinkage. This allowed them to determine the negative effect of epoxy resin content on the stability of the calcia-based ceramic, with solid loading acting to decrease linear shrinkage and epoxy resin content having the opposite effect at constant loading (Tables 3 and 4) [73,123].

Thermal conductivities can generally be, as a first approximation, assumed from prior work based on the material of the ceramic shell [124,125]. Alternatively, more accurate thermal conductivity values can be derived from thermal diffusivity measurements which can be directly taken through the laser flash method, during which one side of

Table 3

Effect of solid loading on the linear shrinkage of the dried green and sintered bodies derived from the 16 wt% epoxy resin slurries (redrawn with permission from Ref. [73]).

Solid loading (vol%)	Shrinkage (%) from mold size/green body	Shrinkage (%) from green/sintered body	Shrinkage (%) from mold size/sintered body
40	5.26	10.83	15.52
42	4.53	10.34	14.40
44	4.38	9.57	13.53
46	3.94	9.04	12.62
48	3.62	7.98	11.31

Table 4

Effect of epoxy resin content on the linear shrinkage of the dried green and sintered bodies derived from the 44 vol% slurries (redrawn with permission from Ref. [73]).

Epoxy resin content (wt%)	Shrinkage (%) from mold size/green body	Shrinkage (%) from green/sintered body	Shrinkage (%) from mold size/sintered body
12	4.09	8.45	12.19
14	4.31	9.13	13.05
16	4.88	11.03	15.37
18	5.77	12.34	17.40

the sample is subject to an energy input from a laser after which a temperature rise is measured against time at the opposite side [126]. This method does, however, have some limitations, particularly with insulating and large-grain heterogeneous materials due to the generation of large temperature gradients formed near the heated surfaces [127,128]. In order to overcome these large thermal gradients, step heating methods have been used to limit energy intensity while increasing exposure time to decrease the sensitivity of thermal diffusivity estimation [129].

6. Concluding remarks

The viability of shells and cores for the investment casting of nickel superalloys depends on several factors, including the strength of the mold relative to the solidifying alloy, thermal shock resistance, dimensional stability, leachability, reactivity, permeability, and cost. Future research into new ceramic mold materials, processing, and characterization methods as well as developments to already existing techniques should be based around these particular properties to improve the interactions that occur at the mold-metal interface and mitigate the aforementioned limitations of current casting methods. Based on the findings of this review, the following conclusions can be drawn.

- Oxides represent the most promising base materials for ceramic molds as a result of their chemically inert nature, which is critical to avoid reactions between the ceramic and reactive elements in the melt. With that being said, pure forms of these oxides, or any pure material studied to this point, have not been found to be entirely sufficient to satisfy the extensive requirements of a ceramic mold for the casting of high-performance superalloys. Because of this, it is likely that mixtures and/or composite structures of various ceramic materials will exhibit the most viability for ceramic mold applications.
- More work is necessary to analyze the reactions taking place during processing, particularly at the mold-metal interface. Understanding of how reactive elements in the melt interact with the ceramic mold is still not completely developed, limiting the capability to successfully mitigate this problem. Furthermore, existing literature about these reactions are relatively inconsistent with one another and are often predicated on subjective statements about reactivity.

More concrete, quantitative data is needed to better understand how superalloys react with the ceramics during processing and to model the reactions occurring at the ceramic/metal interface.

- Additive manufacturing (AM) is likely to play a major role in the future development of ceramic casting shells and cores. To start, additive manufacturing techniques provide reduced tooling cost, material waste, and start-up times when compared to traditional mold-forming methods. Utilizing AM in the mold forming stage of investment casting has been shown to improve lead times by up to 89% and reduce production costs by up to 60% [68]. Beyond this, it offers significantly more dimensional and structural control, allowing for selective manufacturing of shell thickness and permeability to preferentially address susceptible zones in the shell. Additive manufacturing also allows for manufacturing flexibility to more precisely form layered shell components. This enables the generation of products with functional gradients to utilize non-reactive and high-performance outer layers while maintaining a lower cost, more leachable core body.
- Shrinkage and creep, which occur in the mold in large part during sintering and casting, are critical factors in maintaining structural and dimensional stability in the ceramic. There have been a few methods which have shown promise in reducing the shrinkage and creep observed in the mold, which could be important for applicable future projects. The first of these methods is through the use of additives such as magnesia and alumina which, when used in the production of low-cost alumina cores, were able to minimize shrinkage to levels below 1%. Additionally, a freeze-drying process as opposed to the standard air drying showed significant success in minimizing shrinkage and suppressing the formation of cracks that may result.

Declaration of Competing Interest

The authors report no declarations of interest.

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