04 Aug 2004

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ABSTRACT

Ice patterns generated by rapid freeze prototyping or a molding process can be used to make ceramic investment molds for metal castings. Due to the use of ice, the ceramic slurries must be poured around the pattern and cured at sub-freezing temperatures. Success of this process depends greatly on the mold strength after the gelation of the slurries. This paper describes the experimental results of the mold strength after the gelation of the slurries under different compositions. The parameters considered include mixing time, alumino-silicate vs. fused silica ratio, volume of binder, and volume of catalyst. The strength of the gelled slurries is examined by breaking test bars on a four-point bending apparatus. Weibull modulus for each trial is calculated based on the breaking strength from four-point bend tests. Analysis of variance for breaking strength and Weibull analysis is performed to evaluate the significance of the effect of each parameter. The casting of a bolt is used to demonstrate that metal castings of complex geometry can be fabricated using investment casting with ice patterns.

1. Introduction

Every foundry has shell cracking problems in investment casting as a result of mechanical stress. To avoid the shell cracking problems, the investment casting process and the materials used must be strictly controlled. New approaches to improve the performance of investment casting process are constantly being sought. Wax is the most commonly used material to make patterns in investment casting [1, 2]. Stresses applied by wax as it is heated during wax removal appear to be the major cause of shell cracking. The ceramic shell must withstand pressure from expanding wax as it is heated during the wax removal stage as well as survive the rigors of handling during the shell building process. Otherwise, cracking occurs. By contrast, ice exhibits a contraction upon melting. Use of ice patterns may alleviate investment shell cracking as illustrated in Figure 1.

Freeze Cast Process (FCP) is an investment casting process patented by Yodice in 1991 [3]. In this process ice patterns instead of wax patterns are used to make metal parts. Yodice and others have demonstrated the feasibility and advantages of investment casting with ice patterns [4-7]. The advantages of FCP over the competing casting processes include low cost, high quality, and fine surface finish. These strengths make FCP a significant alternative to the traditional investment casting for production of quality near-net shape castings at reasonable costs. In FCP, ice patterns are made by freezing water in a mold box. Alternatively, Rapid Freeze Prototyping (RFP), a solid freeform fabrication technique, can build a three-dimensional pattern directly from a CAD model by freezing water droplets layer by layer [8, 9]. Ice patterns generated by RFP have been used in the investigation of investment casting to fabricate metal

parts with promising results [10-15]. Due to the use of ice, an alcohol based slurry system must be used for the investment mold because molding is done below the water freezing point. Success of this process depends greatly on the mold strength after the gelation of the slurries. The ceramic mold materials used in this study exhibit specific characteristics because of the low temperature environment. Although investment casting with ice patterns has been developed for quite some time, few publications in the literature discuss the properties of ceramic molds suitably formulated to be made in a low temperature environment.

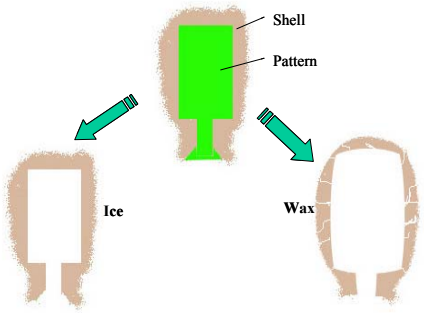

Figure 1: Use of ice patterns may alleviate investment shell cracking.

In this paper, the selection of the ceramic powder, binder and catalyst material for ceramic slurry in the mold making process is discussed. The experimental results on the mold strength after the gelation of the slurries with different compositions are described. The parameters considered include mixing time, alumino-silicate vs. fused silica ratio, volume of binder, and volume of catalyst. The strength of the gelled slurries is examined by breaking test bars on a four-point bending apparatus. The degree of reliability of test bars is determined by Weibull distribution and modulus. The casting of a bolt is used to demonstrate that metal castings of complex geometry can be fabricated using investment casting with ice patterns.

2. Choice of Material for Low-Temperature Investment Casting

Some materials used for investment casting with ice patterns should have different features from those used for regular investment casting with wax patterns [16]. For example, the binder solution for investment casting with ice patterns should contain no water and should not freeze at temperatures slightly below the freezing point of water. Discussed in this section are materials for binder, ceramic powder and catalyst used to make molds for investment casting with ice patterns.

2.1 Ceramic materials

It is well known that the slurry is made of the mixture of binder and ceramic materials. Therefore, ceramic materials play an important role in successful mold (shell) making. In general, ceramic materials are used in a very wide range of combinations and include silica sand, alumino-silicates, alumina, fused silica, and zirconium silicate. Suitable choice of the ceramic materials can lead to smooth surface finish, high accuracy, and good property of the metal castings. The following factors need to be considered when choosing the ceramic materials: specific gravity, linear expansion coefficient, chemical composition, cost, and application. For example, a ceramic material usually has several particle sizes with a certain mixing ratio for shell making. The ratio of fine/medium/coarse powder is critical for shell quality. Because of our interest in small parts made by investment casting with ice patterns, the alumino-silicates having

the grain size of 200 mesh was first chosen. But the molds made have exhibited a low strength and can easily crack as shown in Figure 3(a). So fiber reinforced fused silica was employed in this study to derive crack-free molds as shown in Figure 3(b). The detailed results will be discussed later.

(a) Without fused silica (b) With fused silica

Figure 2: Molds made with and without fiber reinforced fused silica.

2.2 Binder

Binder is another major slurry material. It is mixed with ceramic material to make the slurry. For low-temperature investment casting, the binder solution should have good fluidity at a sub-zero temperature, and the corresponding mold or shell made must have good surface finish, high accuracy and high strength. These are the criteria used in choosing binder materials in our application. In general, there are three kinds of binder materials that can be chosen: water glass, silica gel, and ethyl silicate. Only ethyl silicate satisfies all the above requirements and was used in our study. Pure ethyl silicate can be used to produce a foundry binder but it is more usual to employ a condensed or concentrated form containing certain amount of silica, say 40% by weight. Ethyl silicate 'as received' has no binding properties, but must be chemically decomposed by reacting with water, i.e., hydrolyzed [2]. The reaction produces alcohol and silica in an active state. Since ethyl silicate is not soluble with water, the reaction only occurs on the interface and thus is slow. Alcohol is soluble with both ethyl silicate and water.

2.3 Catalyst

A catalyst is required to shorten the gelling time of the slurry (mixture of binder and ceramic material) for low-temperature investment casting. Otherwise, it will take days or even longer for the slurry to gel. In general, the gelling time mainly depends on temperature, binder composition, and pH value. The effect of pH value is more significant than the effect of the other two factors. The slurry is most stable when pH value is equal to 2, thus the gelling time is the longest when pH=2. On the other hand, the slurry is most unstable and the corresponding gelling time is the shortest when the pH value is between 5.0 and 6.0. When pH value is less than 1.0, the slurry is also unstable. The aim of adding a catalyst is to change the pH value of the slurry from the range where the slurry is stable to the range where the slurry is unstable. The catalyst can be either acid (to change pH value towards 1.0) or alkaline (to change pH value towards 6.0). The results in ref.[7] show that triethanolamine has a good performance when used as a catalyst.

2.4 Slurry System

Slurry contains ceramic powder, binder and catalyst. The ratio among these three components is important to the performance of the slurry system, the building of ceramic shell or mold, and consequently the quality of castings. Therefore, a right mixing ratio among the three components is critical to controlling the accuracy and surface finish of castings [2].

Based on the discussion above, the following materials were chosen: mixture of alumino-silicates (M47-200ICC, Ransom and Randolph) and fiber reinforced fused silica (NALCAST, Nalco Chemical Co.) as ceramic powder, alcohol-based pre-hydrolyzed ethyl silicate (binder #18, Ransom and Randolph) as binder, and mixture of triethanolamine and ethanol (1:1.5 volume ratio) as catalyst. The particle fineness of alumino-silicates is 200 mesh. The particle size distribution of fused silica is shown in Table 1.

Table 1. Particle size distribution of fused silica.

Particle size (mesh)	<50	50-100	100-200	200-Pan
Percentage (%)	3.0-7.0	4.0-14.0	12.0-22.0	60.0-80.0

3. Experimental Procedure

Besides the materials mentioned above, mixing time is also considered in this study because mixing time significantly affects the evenness of the slurry. Therefore, four parameters total were chosen in this study: catalyst (mL), binder (mL), ceramic powder (g), and waiting time (min). Four levels for each of these parameters were selected. To reduce the trial runs, Taguchi method was employed and an L16 orthogonal array is derived. The experimental conditions and corresponding solid loadings (Vol. %) are listed in Table 2.

Table 2. Taguchi experimental matrix and corresponding solid loading.

Experiment No.	Mixing Time (min)	Alumino-silicate/Fused silica (g)	Binder (mL)	Catalyst (mL)	Solid Loading (vol.%)
1	1.5	350/0	130	7	49.18
2	1.5	325/25	140	8	47.24
3	1.5	325/50	150	9	47.17
4	1.5	325/75	160	10	47.11
5	2	350/0	140	9	47.08
6	2	325/25	130	10	48.63
7	2	325/50	160	7	45.95
8	2	325/75	150	8	48.93
9	3	350/0	150	10	45.31
10	3	325/25	160	9	43.95
11	3	325/50	130	8	50.71
12	3	325/75	140	7	50.74
13	4	350/0	160	8	44.11
14	4	325/25	150	7	45.78
15	4	325/50	140	10	48.63
16	4	325/75	130	9	52.14

Test bars were made by pouring the ceramic slurry into ice molds, gelling the slurry and ultimately melting ice molds. The geometry and the dimensions of the designed test bar are illustrated in Figure 3. The design of the test bar was based on the ASTM standard C1161-02c and the work of Baratta, and modified in consideration of the low strength of the gelled slurry [17-19]. The tensile side of the test bar was against ice with no post-processing done to it. After the gellation, the test bars were fired like firing a mold. The length and thickness of each bar

were measured and recorded. The samples were then fractured using the four-point bend apparatus.

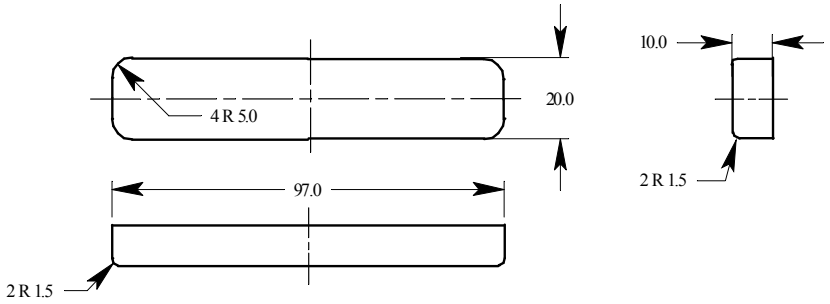

Figure 3: Dimensions of the molded test bar.

A four-point bend apparatus adapted to an Electronic Universal Sand Strength Machine (Simpson Technologies Corporation) was used to examine the properties of ceramic mold materials. The four-point bend apparatus subjected the tensile portion of the sample to a uniform stress over a specified region. A fully equalized fixture was built following the concepts of error reduction in ceramic testing proposed by Baratta for technical ceramics [19]. Data for bars that failed at or outside the four load points were considered suspect and omitted from the statistical analysis. For each test, about fifteen to twenty bars were prepared. Weibull modulus was calculated based on the four-point test results.

Table 3. Experimental results from the four-point bend test.

No.	Average breaking strength (MPa)	Standard deviation (Mpa)	Weibull modulus
1	0.370	0.086	4.49
2	0.382	0.052	7.62
3	0.533	0.136	4.03
4	0.459	0.066	7.41
5	0.304	0.040	8.10
6	0.353	0.063	5.89
7	0.412	0.106	4.01
8	0.394	0.061	6.78
9	0.238	0.027	9.20
10	0.256	0.032	8.53
11	0.341	0.030	11.12
12	0.408	0.073	6.00
13	0.246	0.031	8.28
14	0.307	0.054	5.96
15	0.354	0.030	12.55
16	0.511	0.116	4.50

4. Results and Discussion

4.1 Analysis of variance (ANOVA)

After performing the four-point bend test, the breaking strength and Weibull modulus were derived as shown in Table 3. In order to study the significance of the effect of each

parameter, analysis of variance was employed to quantitatively estimate the relative contribution each parameter makes to the breaking strength and Weibull modulus.

ANOVA uses sum of squares to quantitatively examine the deviation of the control factor mean response from the overall experimental mean response [20]. The total variation in the measurements can be divided into two separate components: the variation due to the effects of the control factors and the variation due to the errors. The significance of the individual control factors is quantified by comparing the variance between the control factor effects against the variance in the experimental data due to random experimental errors and the effects of unrepresented interactions. The F-ratio can be calculated as a ratio between the control factor effect variance and the experimental error variance as follows:

$$F = \frac{MSA}{MSE} \tag{1}$$

The effect variance for a control factor is

$$MSA = \frac{\frac{1}{n}\sum_{i=1}^{K}\left(\sum_{j=1}^{n} y_{ij}\right)^2 - \frac{1}{Kn}\left(\sum_{i=1}^{K}\sum_{j=1}^{n} y_{ij}\right)^2}{K-1} \tag{2}$$

The experimental error evidence for the control factor is

$$MSE = \frac{\sum_{i=1}^{K}\sum_{j=1}^{n}\left(y_{ij} - \overline{y}_i\right)^2}{K(n-1)} \tag{3}$$

where n is the number of replicates within each of K factor levels, y_{ij} is the *jth* observation within factor level i, $\overline{y}_i$ is the mean of observations within factor level i. A P-value, which is a measure of evidence against the null hypotheses, can be obtained corresponding to the calculated F-ratio. Null hypothesis is typically a statement of no difference or effect. A P-value close to zero indicates that the null hypothesis is false, and that a difference is very likely to exist. P-values close to 1 imply that there is no detectable difference for the sample size used. A P-value of 0.05 is a typical threshold used to evaluate the null hypothesis.

Tables 4 shows the analysis of variance for the breaking strength and Weibull modulus. It can be seen that mixing time, the amount of binder, and the ratio of alumino-silicate vs. fused silica affect the breaking strength significantly. Among these three parameters, the influence of the alumino-silicate/fused silica ratio is most significant. The effect of the amount of catalyst on the breaking strength is insignificant. The effect of all the four parameters on the Weibull modulus is insignificant.

Table 4. Analysis of variance

Source	Breaking strength		Weibull modulus	
	F-Ratio	P-Value	F-Ratio	P-Value
Mixing time	27.12	0.000	2.44	0.146
Alumino-silicate/Fused silica	182.69	0.000	0.35	0.566
Binder	14.02	0.000	0.01	0.940
Catalyst	0.01	0.907	2.79	0.123

4.2 Breaking strength

The standard formula for the strength of a beam in four-point-1/4 point flexure, where the load points are spaced ¼ of the span from the rest points, is as follows:

$$S = \frac{3PL}{4bd^2} \tag{4}$$

where P is breaking force, L is span length, b is specimen width, and d is specimen thickness. Table 3 shows the average breaking strengths and corresponding standard deviations for each trial. It can be seen that the values of breaking strength are in a large range.

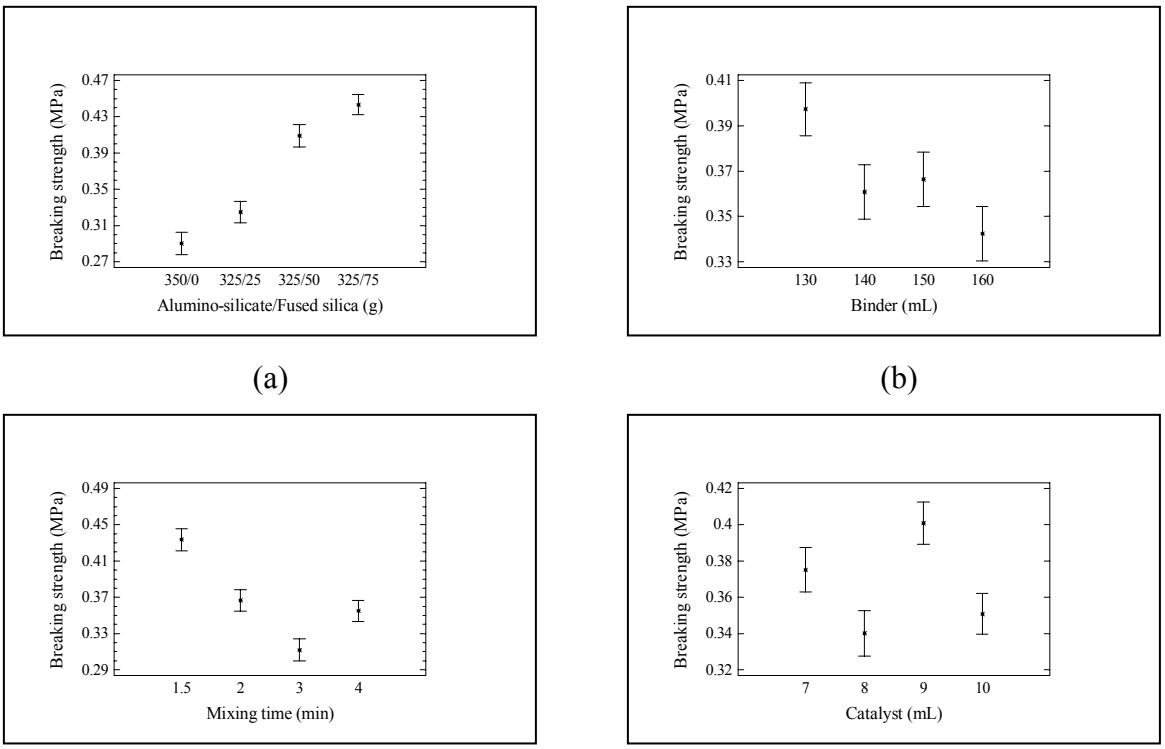

Figure 4: Effect of different parameters on breaking strength.

Figure 4(a) shows the effect of the amounts of alumino-silicate and fused silica with fiber added on breaking strength. It can be seen that breaking strength increases with increase in the amount of fused silica. This can be explained as follows. First, the increase of the amount of fused silica increases the solid loading and decreases the amount of hydrolysate in the slurry. The amount and volume of micro-voids and micro-cracks reduce with the increase of solid loading, making the shell or mold denser and thus improving the strength. Second, fused silica contains large proportion of relative fine particles (200 mesh to Pan), compared with alumino-silicate particles (200 mesh). Packing efficiency improves so that it makes more effective use of the gel or bond phase. Figure 4(b) shows the effect of volume of the binder on breaking strength. In general, breaking strength decreases with increase in the amount of the binder because of the associated decrease in solid loading. The evaporation of large amount of solvent and alcohol can result in volume shrinkage in the mold material and generation of micro-voids and micro-cracks, thus decreasing breaking strength. The breaking strength when the volume of binder is 140 mL is

a little lower than that when the volume of binder is 150 mL. This is because the effect of the alumino-silicate to fused silica ratio is more significant than that of the amount of binder, as indicated by the ANOVA analysis. Figure 4(c) demonstrates the effect of mixing time on breaking strength. Overall, break strength decreases with increase in mixing time. This is because mixing beyond the onset of gelling mechanically destroys the network. Figure 4(d) demonstrates the effect of the amount of catalyst on breaking strength. No trend can be found because the effects of mixing time, amount of binder, and alumino-silicate/fused silica ratio on breaking strength are much more significant than that of the amount of catalyst.

4.3 Weibull distribution

Table 3 shows that there is considerable scatter in the values of breaking strength from the bend test. Due to brittleness of ceramic mold materials, breaking strength depends on the size and geometry of the flaws present [21-23]. Ceramic parts produced from identical materials using identical methods might fail at statistically distributed loads. In order to design ceramic molds with some degree of reliability, Weibull modulus was employed to evaluate the reliability of mold materials. Weibull modulus, m, was obtained by plotting lnln[1/(1-P)] as function of lnσ, performing the linear regression, and calculating the slope of the straight line, based on Equation (5). Better material homogeneity appears as a higher value of Weibull modulus, m.

$$\ln\ln\left[\frac{1}{1-P}\right] = m\ln\sigma - m\ln\sigma_0 + const \tag{5}$$

The probability of failure P is estimated as $n/(q+1)$, where n is the rank order of samples according to strength and q is the total number of samples tested. σ is the rupture stress, and σ_0 is the characteristic stress depending on the distribution function that best fits the data.

At low stresses, a small fraction of samples contain flaws that are large enough to cause fracture; most fail at an intermediate applied stress; and a few contain only small flaws and do not fail until large stresses are applied. For predictability, a narrow distribution is preferred. This corresponds to a large value of m, and more homogeneous material. The corresponding Weibull moduli are listed in Table 3. For each individual trial, a large standard deviation of breaking strength results in a small Weibull modulus. The reliability degrades because of the presence of flaws inside mold materials. Weibull modulus depends on the amount, size, and the distribution of existing micro-voids and micro-cracks. The compositions for trial No.11 and No.15 give higher Weibull moduli.

4.4 Investment casting with ice patterns

Based on experimental results and analyses above, the composition for trial No.11 was selected to make ceramic slurries. The composition worked very well in the investment casting with ice patterns. Several parts including a gear, a coin and a bolt were made to demonstrate that metal castings of complex geometry can be fabricated using investment casting with ice patterns. Figure 5 shows the metal casting of a bolt from an ice pattern.

5. Conclusions

This paper describes the experimental results of breaking strength and Weibull modulus of the test samples generated in a low temperature environment. The test samples are made of mold materials of ceramic slurries for investment casting with ice patterns. The parameters considered include mixing time, alumino-silicate/fused silica ratio, volume of binder, and

volume of catalyst. Analysis of variance shows that the mixing time, amount of binder, and alumino-silicate/fused silica ratio affect the breaking strength significantly. The effect of catalyst amount is insignificant in affecting breaking strength. Breaking strength increases with increase in the amount of fused silica used in the ceramic materials but decreases with increase in the amount of binder or the amount of mixing time. Weibull modulus was used to obtain a set of parameter values that leads to reliable experimental results. Sound molds have been made to demonstrate successful fabrication of metal parts from ice patterns.

Figure 5: Metal casting of a bolt.

Acknowledgement

The authors gratefully acknowledge the financial support from the National Science Foundation grants (DMI-0128313, DMI-0140625 and DMI-0321712). The authors would also like to thank P. D. Jackson for taking pictures for fractography.

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