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Composite polymer derived ceramic system for oxidizing environments

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Abstract Preceramic polymers and expansion agents are being investigated to produce composite ceramic coatings for oxidation protection of metallic substrates. In this paper, we present results of a systematic approach to selecting the preceramic polymer and expansion agents and the optimization of the processing parameters to produce composite ceramics. Six commercially available poly(silsesquioxane) polymers and a polysiloxane were studied. In addition, several metals and an intermetallic were considered as potential expansion agents. Based on this study, the most desirable polymer/expansion agent combination and optimal processing parameters have been identified.

Introduction

For the past two decades, the processing of ceramics and ceramic composites using polymeric precursors has been gaining recognition for the advantages it offers over traditional ceramic processing. These advantages include lower processing temperatures and highly tailorable compositions and microstructures [1–4]. The breadth of applications for these materials is slowly being realized: thermal and environmental barrier coatings [5–8], porous ceramics [9] and ceramic foams for filters [10], reinforcement [11], catalytic microreactors [12], fabrication of high temperature MEMs devices [13–16], bulk composites [17–19], and as joining material for ceramics and other applications [5, 20]. The focus of this research is to systematically determine the constituents of a composite system processed from filled preceramic polymers for protection in an oxidizing environment. The anticipated application for this system is as an oxidation and coking corrosion protection coating on stainless steel.

Preceramic polymers are organometallics that lose their organic components upon pyrolysis to form an amorphous or nanostructured ceramic. There are many types of preceramic polymers now available on the market. Precursors to carbides, nitrides, and oxides are used to form such ceramics as SiC, B_4C, TiC, Si_3N_4, BN, AlN, Al_2O_3, and SiO_2 [1, 3]. Because of the need to form an oxidation and corrosion resistant system, this investigation has focused on the siloxane set of precursors and a subset of this family: silsesquioxanes. Both have high oxygen content and are precursors to SiO_2, Si–O–C, and Si–O–C–N. Siloxanes are linear polymers while silsesquioxanes are highly crosslinked three-dimensional structures such as cages, ladders, and randomly structured networks (Fig. 1). The advantage of this structure is that the starting polymer is already highly cross-linked, which results in a higher ceramic yield upon pyrolysis.

Most preceramic polymers are thermosets and can be liquid or solid at room temperature. They crosslink at relatively low temperature, 100–200 °C, and then are pyrolyzed at higher temperatures, anywhere from 450 °C up to 1500 °C. At temperatures ranging from 1200 °C to 1600 °C crystals will nucleate and a ceramic nanostructure

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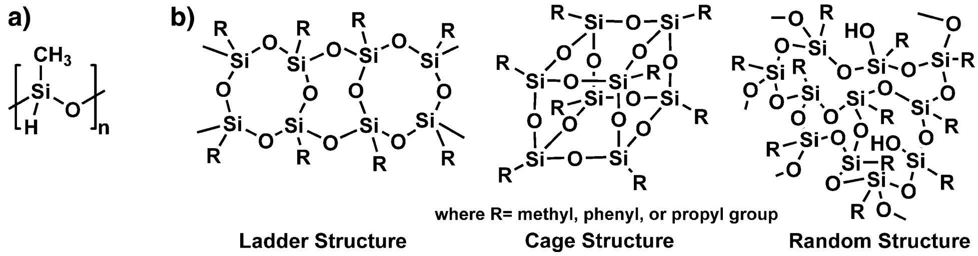
Fig. 1 Structure of (**a**) a linear polysiloxane, poly(hydridomethylsiloxane), versus (**b**) three structures for 3-D silsesquioxanes [21]



develops [22]. The ceramic yield is defined by the following equation:

$$\alpha^{P} = \frac{\text{mass}_{\text{pyrolyzed ceramic}}}{\text{mass}_{\text{polymer precursor}}} \tag{1.1}$$

It is essential to have a high ceramic yield, greater than 75%, when choosing preceramic polymers in order to ensure a low weight loss and shrinkage of the polymer upon pyrolysis. High ceramic yield polymers are easier to densify and have lower tendency to form cracks when applied in constrained geometries (e.g. coatings or composites).

The biggest challenges when using these systems is to overcome the shrinkage of the polymer during pyrolysis, which can be greater than 50% by volume, and to avoid the formation of pores. Furthermore, residual stresses caused by constrained or differential shrinkage and porosity cause defects and cracks in coatings that can lead to poor coating coverage or delamination. Greil et al. [3] developed a method of ''active-filler-controlled-pyrolysis'' in which elemental or binary metal filler particles are selected so that they react with the pyrolysis atmosphere, expand, and thereby compensate for the shrinkage of the polymer. The volume change of filler metal as a result of the reaction with the surrounding environment can be calculated using the following equation

$$\frac{\Delta V}{V_{o}} = \alpha^{EA}\beta^{EA} - 1 \tag{1.2}$$

where $\alpha^{EA} = \frac{\text{mass of reaction product}}{\text{mass of expansion agent}}$ and $\beta^{EA} = \frac{\text{density of expansion agent}}{\text{density of reaction product}}$

This paper outlines the selection of a preceramic polymer matrix material and several expansion agents suitable for producing ceramic composite coatings. Processing parameters such as reactive atmosphere and heating rate are also addressed.

Materials and experimental techniques

Evaluation of preceramic polymers

Six commercially available silsesquioxanes and a derivative of a linear siloxane were studied based on these initial property goals. The polymers are: methylsilsesquioxane (MSQ), phenylsilsesquioxane (PSQ), phenylmethylsilsesquioxane (PMSQ), and phenylpropylsilsesquioxane (PPSQ) all obtained from Gelest, Inc. (Morrisville, PA, USA). Two silsesquioxane polymers were purchased from Starfire Systems, Inc. (Malta, NY, USA): Oxycarbide A and Oxycarbide C. The siloxane used was poly(hydridomethylsiloxane) (HMS-992; Gelest Inc.). A derivative of this polysiloxane, PHMS-OH, was synthesized by substituting –OH groups for the –H side groups as this has been shown to increase moisture stability and enhance wetting on inorganic surfaces (Fig. 2) [23–25]. For comparative purposes, PHMS-OH was dried at 100 °C in air to remove all excess ethanol from synthesis and ground into powder prior to thermal testing. Solid silsesquioxane samples were also ground to powder of < 150 microns before analysis.

Thermal gravimetric analysis (STA 409A; Netzsch GmbH, Selb, Germany) was used to determine the ceramic yield of each of these polymers. TGA was performed for all samples at a heating rate of 1 °C/min up to 1200 °C in three atmospheres: helium (inert), nitrogen, and air. Two polymers, methylsilsesquioxane and Oxycarbide A, were selected to test the effect of heating rate on ceramic yield of the polymer. These tests were run at 1, 5, and 10 °C/min up to 800 °C in air.

Evaluation of expansion agents

Thermal gravimetric analysis was performed on selected metal fillers Al, Cr, Fe, Si, $TiSi_2$ (particle size 10–50 μm), and Ti (particle size < 10 μm) to determine their reaction potential and to determine the effect of heating rate on their conversion to oxide. Powders, excluding titanium, which was too reactive, were attrition milled for five hours in isopropanol to decrease particle size and remove protective oxide surface layers. Particle sizes were reduced to < 10 microns in all cases except Fe, where flakes of ~10–20 microns resulted. Heating cycles of 1 °C/min and 5 °C/min up to 800 °C with a one-hour hold time in air were used for the oxidation studies. Oxidation reaction products were identified using X-ray powder diffraction (Philips PW 1830 X-Ray Diffractometer).

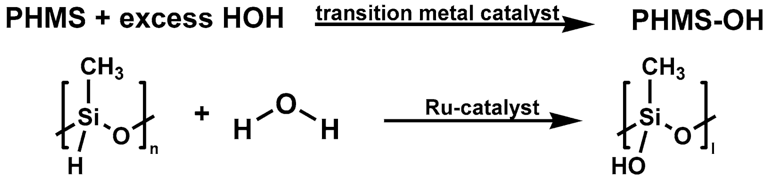


Fig. 2 Synthesis reaction to form poly(hydridomethylsiloxane) derivative PHMS-OH by –OH substitution [23–25]

Results and discussion

Selection of a polymer

There are several criteria to consider when selecting a preceramic polymer for a specific application. The first is that the polymer must have a high ceramic yield on pyrolysis and a minimum of 75% was set for this research. Second, the polymer must be completely pyrolyzed at a temperature below that of the maximum service temperature for the coated substrate. The substrate in this case was AISI 316 stainless steel and a service temperature was specified at 800 °C. Third, the phase formed upon pyrolysis must be desirable for the specified application. Since oxidation and corrosion protection are the main goals of the research, a set of preceramic polymers that produce oxide phases in both oxidizing and inert atmospheres was studied. This includes siloxane and silsesquioxane polymers. In addition, the polymer must be a liquid or soluble in an organic solvent to allow for easy application to the substrate through dip coating. This allows for adjustment of the slurry viscosity to one suitable for dip coating (~20–100 cP).

For all the polymers tested, measured ceramic yields were consistently high, in most cases over 70%, and pyrolysis was complete by 850 °C (Fig. 3). A summary of the polymer weight loss after pyrolysis is presented in Table 1. Ceramic yields in air tended to be lower than those in helium or nitrogen; this is because the organic side groups are volatilized in air. In helium and nitrogen atmospheres, the residual carbon remains in the ceramic solid phase within the system, resulting in a higher yield compared to air. Considering that the potential application for these coatings is as an oxidation barrier, the aim is to create an oxygen-rich coating. This would be most easily done with pyrolysis in air. Two of the commercial polymers showed consistently high yields, even in air. Methylsilsesquioxane and Oxycarbide A had yields of greater than 80% and pyrolysis temperatures lower than 800 °C in air. These two polymers were chosen for further study. The high ceramic yield of these polymers can be explained by their high Si:C ratio. While the methyl side groups are evolved more readily than the larger phenyl or propyl groups, which can remain in the matrix as amorphous carbon, the total mass percentage of carbon lost compared to the remaining silicon is still relatively small.

Another type of siloxane polymer investigated in this work is a poly(hydridomethylsiloxane). This polymer is a byproduct of the silicone industry and more readily available, as well as much less expensive, than the silsesquioxanes that were studied. After substituting the hydrogen side groups and crosslinking, PHMS is believed to resemble silsesquioxanes in its 3-dimensional structure [23]. When a derivative of PHMS, PHMS-OH, was compared to MSQ and Oxycarbide A, it not only exhibited higher ceramic yields, greater than 85%, but also was pyrolyzed below 650 °C in air (Fig. 3, Table 1). PHMS-OH is also easier to integrate into a coating process, since it is a liquid with a viscosity near 80 cP. The silsesquioxanes are solid at room temperature and must be dissolved in an appropriate organic solvent before they can be used for dip coating. Even simpler processing of PHMS is possible since the polymer can be crosslinked in-situ during pyrolysis. If the starting PHMS polymer is used in creating a polymer-filler slurry, then crosslinked at 150 °C under humid air, a similar ceramic yield is achieved without prior synthesis of PHMS-OH. Due to these advantages, PHMS was chosen for all further coating studies.

Selection of an expansion agent

There are several criteria for the selection of a suitable expansion agent, but the main criterion is that the filler material chosen must expand upon reaction with the pyrolysis atmosphere. This expansion criterion is determined based on Eq. 1.2, and, by definition, expansion occurs when $\alpha^{EA}\beta^{EA}>1$ [3]. In addition, the filler should form a dense and stable reaction product, preferably an oxide, to complement the polymer reaction product.

Six expansion agents were chosen for evaluation based on their theoretical expansion during oxidation (Table 2). The calculated values of their volume change and the expected weight gains are listed in Table 2. These six metals were chosen because: (a) they have a large theoretical volume change on oxidation, (b) they are non-toxic, and (c) they are readily available in small particle sizes. The oxidation of Al, Cr, Fe, Si, Ti, and $TiSi_2$ was analyzed using TGA to determine their weight gain upon heating in air (Fig. 4). From these results a percent conversion to a stable oxide phase was inferred. Table 2 compares the expected weight gain for the metal powders based on complete conversion to the corresponding oxide to the actual weight

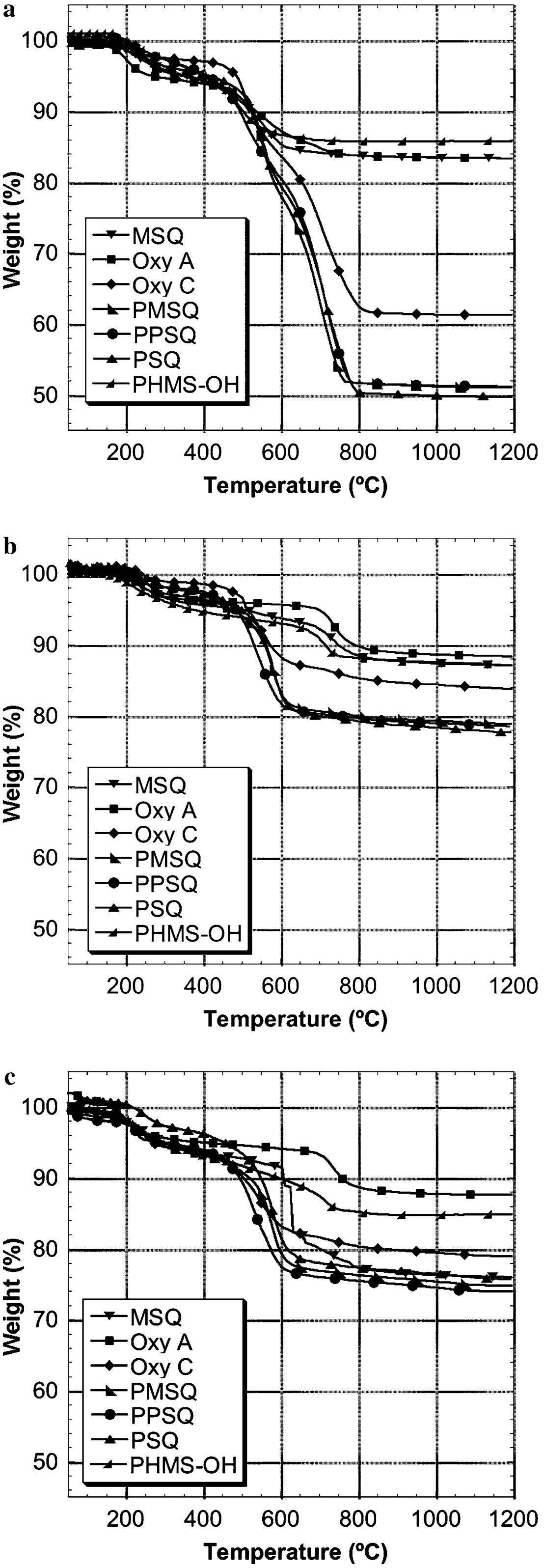


Fig. 3 TGA curves for polymers pyrolyzed in (**a**) air and (**b**) nitrogen and (**c**) helium showing weight loss upon pyrolysis to 1200 °C at 1 °C/min

Table 1 A summary of the ceramic yield and pyrolysis temperature obtained by TGA for the polymers studied. The polymers in italics, methylsilsesquioxane (MSQ), Oxycarbide A, and the PHMS-OH had yields <80% and were chosen for further study

Polymer	Ceramic yield (%)			Pyrolysis temp (°C)		
	Helium	Nitrogen	Air	Helium	Nitrogen	Air
MSQ	*77.2*	*88.0*	*84.4*	825	835	660
Oxycarbide A	*88.2*	*89.1*	*83.9*	*845*	*860*	*765*
Oxycarbide C	80.2	85.0	61.6	820	835	845
PMSQ	76.9	80.8	51.8	695	675	790
PPS()	76.1	80.5	51.6	690	670	805
PSQ	78.1	80.4	50.3	690	655	810
PHMS-OH	*85.4*	*88.3*	*86.5*	*765*	*760*	*620*

gain during analysis. The conversion of Al and Si to oxide was quite poor and the conversion of Cr to oxide was marginal. While some metals were determined, using Eq. 1.2, to be candidates for expansion agents, they ultimately showed oxidation behavior that made them unsuitable for reactive fillers. In part, this was due to a protective oxide layer that forms on the surface of the individual particles during storage and handling. The oxide layer prevents oxygen diffusion to the core of the particles, leaving the bulk of the metal unreacted, which results in insufficient volume expansion for the selected polymer. Based on this, Al and Si were ruled out as expansion agents. For further studies, the remaining powders were attrition milled as this has previously been found to improve reactivity by removal of the outer oxide layer and decrease of the particle size [5]. It was decided to continue to investigate Cr. Although its oxidation was marginal, it has one of the highest $\alpha^{EA}\beta^{EA}$ values (expected volume increase) and Cr_2O_3 has the potential to improve the bonding of the coating to the steel substrate [26].

Effect of heating rate on reaction of components

Once potential polymer-filler systems were determined, the effect of processing variables on the polymer pyrolysis and metal oxidation was investigated. One important processing

Table 2 A comparison of selected expansion agents and their actual weight gains upon oxidation versus their expected weight gains. When $\alpha^{EA}\beta^{EA} > 1$ volume expansion will occur upon oxidation

Element	Oxide	$\alpha^{EA}\beta^{EA}$	Expected Wt. gain (%)	Actual Wt. gain (%)
Al	$A1_20_3$	1.29	89	1.9
Cr	Cr_2O_3	2.01	46	9.6
Fe	Fe_2O_3	1.28	43	40.6
Si	SiO_2	1.88	114	1.5
Ti	TiO_2	1.77	67	48.5
$TiSi_2$	TiO_2+2SiO_2	2.41	92	36.2

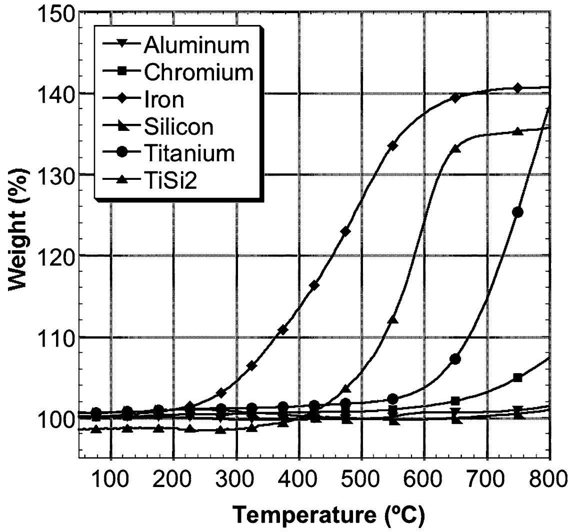


Fig. 4 TGA curve of weight gain of candidate metallic and bimetallic expansion agents due to oxidation in air at 1 °C/min to 800 °C

variable is the heating rate. A study was done to compare polymer decomposition at three heating rates, 1, 5, and 10 °C/min. The polymers used were methylsilsesquioxane and Oxycarbide A. MSQ experienced a decrease in yield as heating rate decreased and Oxycarbide A showed an increase in yield with a decrease in heating rate (Fig. 5). However, the difference in yield between the three heating rates was less than five percent. It was shown that the lower heating rate of 1 °C/min did result in pyrolysis completion at a lower temperature, about 100 °C lower than the sample pyrolyzed at 10 °C/min. In all cases pyrolysis was complete by ~700 °C. These results indicate that the choice of heating rate for the composite coatings would not depend on the polymer pyrolysis but rather on the reactivity of the metal expansion agents.

Therefore, a similar study was conducted to determine the effect of heating rate on the oxidation of the expansion agents Cr, Fe, Ti, and $TiSi_2$. The heating rate had a pronounced effect. An increase in the heating rate caused a decrease in the reaction rate for all four metal powders (Fig. 6). A heating rate of 1 °C/min resulted in the most complete conversion of the metals; for titanium disilicide and iron, oxidation was completed by 700 °C. The exception was titanium; the mass of titanium continued to increase beyond the one-hour hold time. In order to further study the oxidation of Ti, in addition to the 1 °C/min and 5 °C/min TGA runs with one-hour holds, two cycles with 10 °C/min heating and ten-hour hold time were conducted, one to 800 °C, the other to only 700 °C. Figure 7 compares these four curves. It is evident that a higher temperature is needed to oxidize titanium compared to the other expansion agents, as such an increase in temperature from 700 °C to 800 ° C results in a 20% increase in the mass (Fig. 7). Considering the constraints of this study, titanium oxidation was observed to be optimum under the following conditions: 5 °C/min to 800 °C with a hold time of five hours. The oxidation of the metals was the rate-limiting step in the composite coating pyrolysis stage, and, therefore, a slower heating rate must be used when processing the coatings. For our studies, a heating rate of 1 °C/min gives the most complete oxidation of the selected metals.

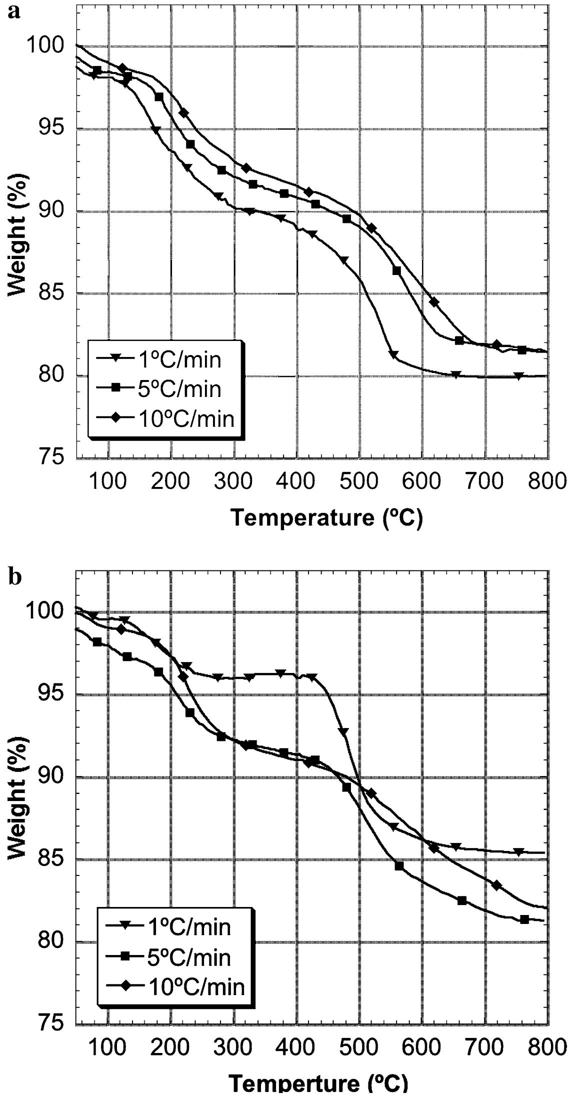


Fig. 5 TGA graph showing the effect of heating rate on (**a**) MSQ and (**b**) Oxycarbide A. Pyrolysis was to 800 °C at 1 °C/min, 5 °C/min, and 10 °C/min in air

Conclusions

The poly(hydridomethylsiloxane) derivative, PHMS-OH, exhibited high ceramic yield in air, ~85%, and complete conversion by 700 °C. This polymer is low in cost and can be tailored more easily during synthesis than the

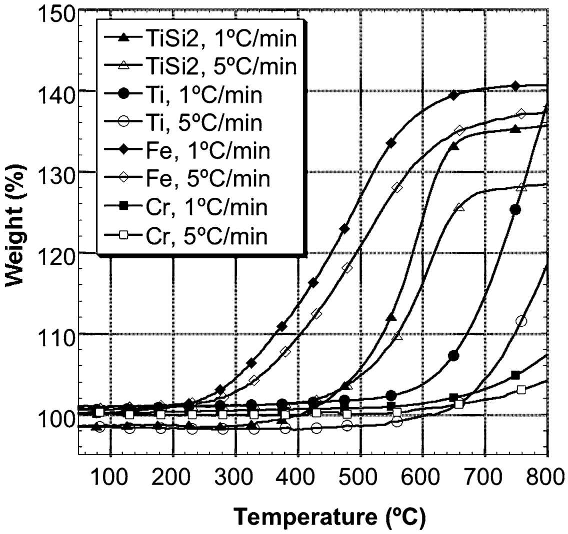


Fig. 6 Effect of heating rate, 1 °C/min and 5 °C/min, on the oxidation of selected expansion agents in air; it can be seen that an increase in the heating rate results in a decrease in the oxidation of the metals

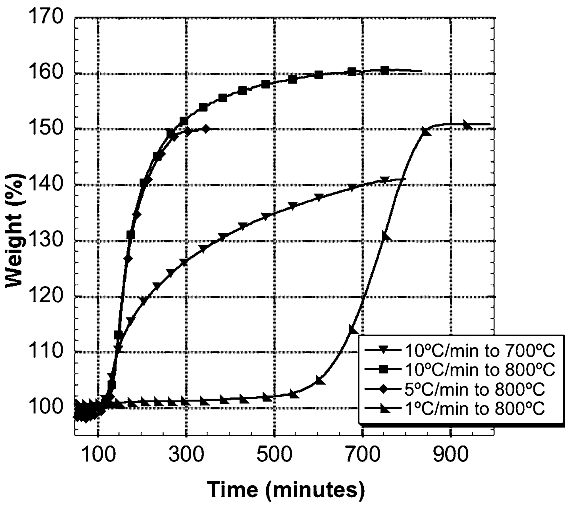


Fig. 7 Effect of heating rate, 1 °C/min and 5 °C/min, and hold temperature on the oxidation of titanium

commercially available silsesquioxanes polymers. PHMS is also a low viscosity liquid suitable for dip coating. As a result of these attributes, PHMS and its derivative are the polymers selected for further study.

The expansion agents Cr, Fe, Ti, and $TiSi_2$ exhibited good conversion from metal to oxide and further examination will be made of their oxidation properties within the PHMS matrix. In general processing studies, it was determined that the reaction of the expansion agents will be the limiting factor in determining heating rate. A heating rate of 1 °C/min with a one-hour hold at 800 °C resulted in the most complete conversion of the metals to oxides.

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