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Determining the oxidation behavior of metal powders during heating through thermogravimetric and evolved gas analysis using a coupled thermogravimetry-gas chromatography-mass spectrometry technique

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ABSTRACT

The oxidation behavior of a fine Ni superalloy (NiSA) powder, Inconel 625, within an alumina support powder during heating has been determined using combined thermogravimetry (TG) and evolved gas analysis (EGA). A gas chromatographic-mass spectrometer (GCMS) was used for EGA. The GCMS was able to semi-quantitatively measure the rate at which air was removed from the furnace due to a He purge, where no pre-evacuation was used. It also was able to measure the effectiveness of a three cycle evacuation and He purge in reducing the oxygen content in the furnace and identify an important alumina off-gassing process that exposed the NiSA powder to H_2O and CO_2. The parallel use of the TG signal was able to quantitatively determine the relationship between NiSA oxidation and relative concentrations of the oxidizing gases created by the differing furnace pre-conditions and the alumina powder off-gassing process. It was concluded that the developed TG-GCMS method can be widely applied to quantitatively study oxygen pick-up in metal powders under industrially relevant processing conditions.

1. Introduction

During powder metallurgy (PM) processing, metallic alloy powders are heated to high temperatures under controlled atmospheres to initiate debinding, sintering and densification. With an increasing emphasis on the use of micron, submicron and nano scale sized powders, contamination of the powders by reaction with the sintering atmosphere and support materials has become increasingly important to consider [1]. This is particularly true for materials containing highly reactive alloying elements such as Al, Cr, Mn and Ti.

In the particular case of the PM sintering of steels, a number of studies have examined the influence of sintering atmosphere on the surface oxide present on alloyed powders [2–8]. The emphasis of this work has been placed on determining atmosphere conditions that would lead to a reduction of Cr and Mn based oxide films present on the surface of the as-processed powders, in order to enhance sintering. Some of these investigations have used post-sintering chemical and microstructural analysis to infer the influence of sintering atmosphere. Other studies have used in-situ thermogravimetric analysis (TG) to better understand the time-temperature mass change of the sample due to reduction/oxidation reactions resulting from the furnace atmosphere.

The current material of interest for this study is a Ni superalloy (NiSA) powder. The sintering behavior of Ni-based superalloys has been studied by a number of researchers over the last 25 years [9–22]. The focus of these investigations has been to develop sintering profiles that are capable of achieving high density components with acceptable mechanical properties. Unlike the sintering of PM steels, a detailed study of the influence of sintering atmosphere on superalloy PM materials has not been reported in the literature as far as the authors are aware. This aspect of processing superalloys is important given the fact that their compositions include measureable amounts of reactive metals including Al, Cr, Mn and Ti.

The overall objective of this research is to develop advanced thermal analysis tools and techniques and apply them to a study of Ni based superalloy powder injection molded (PIM) part processing. The processing steps of interest include thermal debinding, pre-sintering, cleaning and sintering. During the thermal debinding stage, the binder system originally used to fluidize the metal powder for injection molding is removed from the part through melting

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Table 1
List of samples.

Chemical Name			Source		Mole Fraction Purity		
Helium			Air Liquide		0.99999		
Alumina powder			Almatis GmbH		0.999		
Inconel 625			Sandvik Osprey		Conforms to AMS 5599		
Chemical Composition Alloy Inconel 625 (wt%)							
Ni	Cr	Fe	Mo	Nb	Ti	Al	C
Bal.	22.0	≤5	9.0	3.5	≤0.4	≤0.4	≤0.1

and evaporation. Alumina powder is used to give structural support to the PIM part as it loses binder and to aid in wicking the binder [23]. Removal of all binder phases too quickly can result in distortion and cracking of the part while residual binder phases can contaminate and hinder sintering if present post-debind. Therefore, a thorough understanding of the de-binding stage is critical to the success of the PIM process [23]. The specific objective of the current work is to perform an in-depth analysis of the role of furnace atmosphere and presence of alumina during the debinding process on the superalloy powder itself, i.e. the binder was not used in these experiments to reduce the complexity of interpretation.

While TG work applied to sintering has been capable of providing detailed insight into the process, the inability of obtaining parallel in-situ measurements of the composition of the gas atmosphere within the furnace limits its capability. TG analysis coupled with measurements of evolved gas using mass spectrometry (MS), Fourier-transform infrared spectroscopy (FTIR) or gas chromatography (GC) have proven to be very effective in the study of decomposition gases in organic and inorganic materials [24–32]. A primary goal of this research was to develop a methodology which utilized the EGA approach, in this case using GCMS, to determine the changing furnace gas composition as a result of reactions with a metal powder. The combined use of TG and GCMS has the potential to simultaneously determine the extent of oxidation of a metal powder but also the reaction mechanisms involved.

2. Experimental

2.1. Materials

The characteristics of the NiSA and alumina powders used in this study are typical of those used in the powder injection molding (PIM) industry [23] and are listed in Table 1. The superalloy powder described herein as NiSA was Inconel 625 with a particle size of 22 μm, obtained from Sandvik Osprey. The alumina powder was obtained from Almatis GmbH at 0.999 mol fraction purity. Helium gas from Air Liquide with 0.99999 mol fraction purity was used for the TG-GCMS experiments.

2.2. TG-GCMS procedure

The temperature-dependent off-gassing and oxidation behavior of the alumina and NiSA powders were studied using a commercially available thermogravimetry – gas chromatography/mass spectrometry instrument herein called a TG-GCMS. The ultimate goal of this work was to determine the oxidation behavior of a fine metal powder in the context of a PIM thermal debinding operation, where the furnace atmosphere is nominally an inert gas environment. The arrangements of interest are illustrated in Fig. 1 as a schematic of the TG crucible and powders studied, with Fig. 1d giving an approximation of a thermal debinding operation.

To simulate an as-moulded PIM component being debound in alumina powder, loose NiSA powder was poured into an indentation in the alumina powder bed and then covered with more alumina powder. This alumina and NiSA powder arrangement was contained in an open alumina crucible with a maximum capacity of 2 g or 3.4 mL (empty crucible dimensions shown in Fig. 1a). A Netzsch STA 449 F1 coupled to an Agilent 5975E GCMS was used for TG-GCMS analysis. All TG experiments were performed at atmospheric pressure. The standard uncertainty, u, of the temperature is the larger of 1.5 °C or $u(T) = 0.0025 \times T$. The use of a relatively large volume crucible allowed the embedded article arrangement of Fig. 1d to be constructed using an adequately-sized sample. The level of gas evolution from the powders and oxidation in a nominally inert gas atmosphere was expected to be very small. Therefore gram-sized samples were required to obtain the TG and GCMS results.

Correct interpretation of the influence of the furnace atmosphere and alumina on the oxidation of the NiSA required a series of comparative experiments to first be performed. These included full TG-GCMS measurements obtained on an empty crucible (Fig. 1a), alumina only in the crucible (Fig. 1b) and NiSA only in the crucible (Fig. 1c).

In a full PIM process the green body consists of fine powder embedded in a binder mixture consisting of several organic components. In this case one of the roles of the alumina powder is to wick the organic binders out of the PIM part during heating. In the current study, the binder component was omitted in order to fully develop the methodology and realize the full capability of the TG-

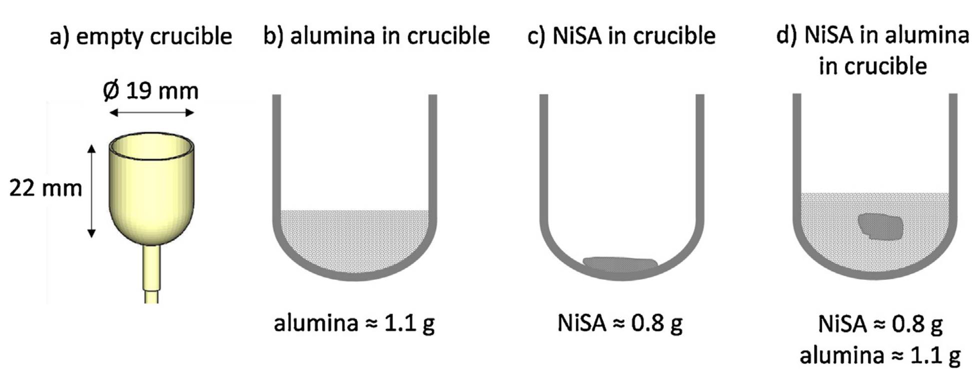

Fig. 1. Schematic of TG crucible, mass of powder used and configuration of powder(s) in crucible.