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Studies on the role of iron oxide and copper chromite in solid propellant combustion

Kumar Ishitha *, P.A. Ramakrishna

Department of Aerospace Engineering, Indian Institute of Technology Madras, Chennai, India

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ABSTRACT

Iron oxide and copper chromite are the known burn rate enhancers used in a composite solid propellant. Lot of research has been carried out to understand the mechanism or location of action of the burn rate modifiers so as to better tailor the burning rate of a composite propellant. The literature is still very confusing in affirming the mechanism. Here, a systematic study has been carried out, by undertaking experiments at varying levels of combinations of the individual components (ammonium perchlorate, which is oxidizer and hydroxyl terminated poly butadiene, which is both fuel and binder) of composite solid propellant. Firstly, thermal gravimetric analysis, differential scanning calorimetry and burning rate measurements on the individual components are carried out to study the effect of iron oxide and copper chromite on the components themselves. It has been noticed that though both iron oxide and copper chromite are effective on ammonium perchlorate, iron oxide is slightly more effective than copper chromite. Also, copper chromite enhanced the binder melt flow, while iron oxide reduced it. These are followed-up by experiments on sandwich propellants, which give greater insight and enables better understanding of the behavior of iron oxide and copper chromite in composite propellants, as these are simple two-dimensional analogue of the composite solid propellants. Finally, experiments are carried out on the composite solid propellants to obtain a holistic understanding of the behavior/location of action of iron oxide and copper chromite in them. These studies are used to explain certain unexplained but observed phenomena, at the same time elucidating the location of action of these burn rate modifiers in composite solid propellant combustion. Based on these observations, it has been proposed that both iron oxide and copper chromite are primarily acting on the condensed phase. These studies are further complimented with experiments to analyze the thermal conductivity measurements of various propellant samples. This is pursued to understand the reason for the differences in burn rate pressure index for the composite propellants with iron oxide and with copper chromite. It has been understood from these studies that the thermal conductivity of a composite propellant is a key parameter, which affects the burn rate pressure index. Literature has never addressed it from this perspective.

1. Introduction

A composite solid propellant burning rate is often modified by the addition of burn rate modifiers to its composition in small quantities (<~3%) [1]. Iron oxide (IO) and copper chromite (CC) are known burn rate modifiers, which are employed in a composite solid propellant when enhancement in the burning rate is desired. In general, much of the literature has been dedicated to understanding the mechanism and location of the burn rate modifiers in the combustion of solid propellants. Table 1, gives a broad overview of the mechanism/action site of these burn rate modifiers, as proposed by various earlier studies. The table should be read as follows. The proposed action site, corresponding to a burn rate modifier, is presented in column one, with the details of the burn rate modifier discussed in the study (whether IO or CC or both IO and CC) themselves given in columns three to five. Column two further elaborates on the proposed mechanism of action for these burn rate modifiers. Again, some of the studies disagree with the proposed action site/mechanism by other studies. To bring out these contradictions among the studies, each of the columns from three to five are divided into two.

A glance at Table 1 and at the review paper by Kishore and Sunitha [43] showed that the proposed mechanisms for IO and CC in the combustion of a composite solid propellant are too varied. In addition to the above discussion, it has been noticed that,

* Corresponding author.
E-mail address: ishikumar86@gmail.com (K. Ishitha).

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Nomenclature

AP	ammonium perchlorate	IO	iron oxide
CC	copper chromite	IPDI	isophorone di-isocynate
DOA	di octyl adipate	*n*	burn rate pressure index
DSC	differential scanning calorimetry	SEM	scanning electron microscopy
HTPB	hydroxyl terminated poly butadiene	TGA	thermal gravimetric analysis

IO and CC when added in a composite solid propellant enhances the burn rate pressure index. This increase in burn rate pressure index is greater with IO than with CC [44]. This is despite the fact (refer Table 1) that, a large portion of the literature proposes the same mechanism of action for both CC and IO. Thus, the main aim of this paper is to explain this aspect of composite propellant combustion. It will also throw more light on the possible location of action of these catalysts in the propellant combustion. For this purpose, experimental studies have been carried out, which are presented further in this paper.

2. Experiments

A typical composite solid propellant (non-metalized) has AP as oxidizer and HTPB as, both fuel and binder. Firstly, experiments are performed to understand the effect of IO and CC on the individual components (AP and HTPB, here) that constitute a composite solid propellant. Then experiments are conducted on sandwich propellants, which is a two-dimensional analog of a composite propellant. Lastly, experiments are carried out with IO and CC in the composite propellants, to bring in the complex interactions that would occur in propellants. Apart from these, quench samples of composite propellants are obtained to study the possible surface structure during combustion. Here, focus is only on non-metalized propellants, so as to eliminate the complex interactions that come into play when another metal component is added. A detailed description of these experiments is presented here. Table 2 shows the source of ingredients used for the experiments reported in this paper.

2.1. Preparation of a pellet

A stainless steel die of circular cross section of 4 cm diameter is used to make AP pellets. AP as obtained is ground into a fine powder of size between 43 and 65 μm in a crucible. Moisture from AP is removed by keeping the powdered AP in a hot air oven at 340 K for 24 h. Around 4.9 g of this dried powder is used to make the pellets using a stainless steel die. A pressure of 200 bar is applied on this die for half an hour with a hydraulic press. The pellets thus obtained are maintained at 302 K in an oven for a day to achieve a uniform temperature throughout the sample. For experiments to study the effect of IO and CC on AP, 1% of these burn rate modifiers (0.05 g) are dry mixed with 4.85 g of AP and same procedure described above is employed to make pellets from this mixture. For sandwich propellant experiments where IO and CC is required to be at the interface of AP and HTPB, pellets of AP are prepared by putting powdered AP of weight 4.85 g under 200 bar pressure for 10 min and then IO/CC of weight 0.05 g is spread evenly on one side of the AP pellet and placed in the die at a pressure of 200 bar for 30 min. The density of pellet is 1900 kg/m^3 which is close to the single crystal density of 1950 kg/m^3. Pellets thus obtained are 2 mm thick. To conduct experiments on the pellets, samples of size 5 mm × 2 mm × 10 mm are obtained.

2.2. Preparation of binder samples

For the experiments to understand the effect of IO and CC on the binder (HTPB), testing has been carried out in a hybrid rocket. The binder in combination with IO/CC is used as solid fuel. The reason behind choosing hybrid rocket testing (to study the effect of IO/CC on the binder) is that the environment in the combustion chamber of a hybrid rocket represents the environment of a solid rocket motor better (as compared to any of the pyrolysing experiments on the binder), due to high heating rates (comparable to the heating rates encountered during solid rocket operation) that can be achieved here. This would ensure that the conclusions drawn from these set of experiments would be more reliable. HTPB (90%) and IPDI (10%) are hand mixed and this mixture is poured into a PVC

Table 1
Proposed mechanism and location of action of IO and CC in the literature.

Action site	Mechanism	With respect to IO		With respect to CC		With respect to both IO and CC*	
		Agree	Disagree	Agree	Disagree	Agree	Disagree
On both AP and binder	Through interaction of perchloric acid with fuel	[2]		[32]		[39]	
	Through interaction of decomposition products of perchloric acid and fuel	[3]		[24]		[39]	
	Through electron transfer process	[4,15]					
	On heterogeneous reactions	[6,8,14]		[25]			
	On homogeneous reactions in the gas phase	[6,8]					
	Through formation of metal ammine complex	[7,15]		[31]			
	In condensed phase	[11]	[5]	[34]		[38,39,41,42]	
	In gas phase	[11,12,14]		[18,19,29]		[38]	
	In diffusion process	[13]		[33]			
	On oxidizer-binder interfacial reactions	[16,18–20]		[27,28]	[18,19]	[21,40,41]	
On AP	On decomposition of perchloric acid	[3,7,10,12]	[2,13]	[23–25,30]		[10,36,37]	
	On decomposition of AP	[14,15]		[22,25–27,29]		[41]	
	On deflagration of AP	[19]		[18–20]			
On binder	On oxidation of the binder	[3,10]		[22,30]		[35,39]	
	On binder	[16,17,21]	[9,12,18,19]	[32,33]	[18,19]	[42]	

* IO and CC are studied individually.