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The effect of sintering activator on the erosion behavior of infiltrated W-10wt%Cu composite

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ABSTRACT

In this paper, the erosion mechanism of infiltrated W-10wt%Cu composites against liquid alumina particles as well as the effect of sintering activators was studied. The fabrication of samples consists of infiltration of copper into sintered porous tungsten skeleton in presence of activators such as Ni and Co. Ni and Co was used as solid state sintering activators. The erosion of prepared specimens observed after the static firing and explained in terms of microstructure, transpiration cooling and erosion mechanism. Chemical analysis of the material after erosion test was obtained using energy dispersive X-ray analysis (EDS). SEM images were employed to identify the microstructure evolution due to erosion. The obtained results show that Composite prepared by Ni additive show about 33% better erosion resistance compare to specimen without additive. Also, presence of sintering activator could enhance transpiration cooling mechanism during erosion. These results discussed based on hardness, contiguity and connectivity.

1. Introduction

W-Cu composites combine high thermal and electrical conductivity of Cu with high strength, high melting point and high erosion resistance of W [1,2]. Excellent thermal shock resistance, especially during firings, cooling ability of copper vapor (or other infiltrant) and less weight than pure tungsten, with much easier machining, are additional benefits of infiltrated compounds [3–5]. On the other hand, Solid or liquid-particle erosion of W-Cu composite materials used in the applications such as propellants and nuzzles is very extreme [6]. The most severe consequent temperature and abrasion problem commonly occurs in such applications [6,7]. In this condition, propellants are admitted into the combustion chamber through the injector. The alumina droplets formation and high convective heat transfer from exhaust gas lead to high erosion of the materials. The environmental conditions under which these materials are experienced are: high temperature, large heat flux levels and highly erosive alumina droplets. Nozzle material made of pure tungsten has failed to provide the needed strength, erosion resistance and thermal shock resistance. This led to Attempt development of a refractory composite based on tungsten-copper system [8].

Hard (solid/liquid) particle erosion implies the removal of material from the surfaces of material due to intensive impact of fast erosive particles. This type of erosion may be described as the collision or crash at high velocity of liquid droplets with a solid surface, which causes the removal of material from the surface [9]. The earliest model of liquid impingement erosion proposed that at the moment of initial impingement, a stress wave generated immediately traveled back from solid-liquid contact into liquid and the liquid exhibited compressible behavior. This model was improved, suggesting that high pressure occurred in liquid impingement erosion and expressed the impact pressure as a function of the density of the liquid, the compressibility of the liquid and the impact velocity of liquid droplet [10]. The erosion mechanism of brittle materials occurs through cracking and chipping and depends on the toughness and hardness of the material [11–13].

W-Cu composites with high tungsten content are producible only by infiltration of a sintered porous skeleton of tungsten [1,14,15]. A green compact of tungsten powder needs a sintering temperature as high as 2150 °C to have sintering densification to 80% of theoretical density [16]. One of the important methods of lowering sintering activation energy is addition of small amount of sintering activator elements. This type of activated sintering has been used in other systems such as Sintering of High Speed Steels in which the phosphorus additive used to promote liquid phase sintering, has been added to these steels in the form of 7 wt% of copper phosphide powder [17]. In the case of W-Cu system, small amounts of transition metals such as nickel and cobalt can lower the activation energy of sintering, allowing a lower sintering temperature [2,18–20]. These elements also help the wetting of copper on tungsten surfaces and improve the infiltration efficiency [21–23].

The main purpose of this study has been to understand the erosion mechanism in general and to characterize the effect of sintering activator on the erosion behavior of infiltrated W-10wt%Cu composite. The

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liquid impingement erosion resistance of prepared composites was characterized by establishing the relationships between erosion rate and transpiration cooling mechanism.

2. Materials and methods

In this work, W (99.95%, 6 μm), Co (99.999%, 2 μm) and Ni (99.999%, 2 μm) powders were used as raw materials. W-Co and W-Ni powder mixtures containing 0.10 wt% of Co and Ni, respectively, were prepared by admixture method. Mixing of initial powders was done in V-blender for 24 h at the rate of 60 rpm. Green compacted pure tungsten, Co doped and Ni doped blocks has been made using Cold Isostatic Press. The densities of these green compacts have been measured by measuring their volume from their dimensions and measuring the weight by precision electronic balance. Subsequently, compacts were sintered to the desired skeleton density of 80 ± 2 vol% under hydrogen atmosphere at various temperatures depending on the composition for each powder mixture (Table 1). Oxygen-free copper strips, 99.99% purity, were cleaned with sulfuric acid and acetone. They were cut to the calculated weight and were placed in a steel 4841 crucible adjacent of the sintered tungsten compact. Infiltration was carried out at 1300 °C for 120 min in hydrogen atmosphere. Sintering and infiltration were carried out at the heating rate of 10 °C/min. Process parameters of three samples are presented in Table 1. The densities of sintered and infiltrated compacts were measured by the Archimedes method.

This study covers the determination of material loss of infiltrated W-10wt%Cu composite due to liquid alumina particles erosion by static firing of the bi-propellant engine. Incident angle of 30° were used to conduct the erosion test for 40 s. The particle velocity was 1200 m/s. The temperature was about 3000 °C. Erosion was measured by means of a profile projector. Optical microscopy, SEM, quantitative metallography and Vickers hardness were used for studying the detailed microstructure of specimens. Also composition of eroded surfaces was characterized using EDS analysis.

3. Results and discussion

The results of density measurement are recorded in Table 2. Based on previous studies, the activating potential of additives is increased in the sequence of Co → Ni [18–20,23,24]. Capability of an sintering activator for low temperature activated sintering of tungsten powder is related to carrier layer deposited around tungsten particles [18–20,23, 24]. An additive which is insoluble in tungsten (based on phase diagrams presented in Fig. 1 [25]) may be segregated to interface of tungsten particles. It provides a high diffusivity transport path for tungsten atoms, so reduces the activation energy for bulk transport of tungsten [18–20]. For Ni additive, carrier layer is a Ni-rich tungsten solid solution [18–20,23]; while for Co additive, W_6Co_7 intermetallic phase acts as carrier layer [22,23,27]. Higher melting point of W_6Co_7 phase in compared with Ni-rich tungsten solid solution phase is another reason for weaker ability of Co to activate, when it compared with Ni. Formation of Ni-rich layer and W_6Co_7 in the Co and Ni-doped composite sample is demonstrated in Fig. 1. Also elemental map of Ni in sintered Ni-doped specimen is given in Fig. 2 that illustrates segregation of Ni around necking zone.

Table 1
Process parameters of three samples.

Sample	Additive (wt%)	Sintering temperature (°C)	Sintering time (h)	Infiltration temperature (°C)	Infiltration time (h)
PW	–	2150	3	1300	2
NW	0.1 Ni	1400	4	1300	2
CW	0.1 Co	1590	4	1300	2

Table 2
The results of density measurement.

	PW	NW	CW
Green density (pct.)	58 ± 1	59 ± 1	59 ± 1
Sintered density (pct.)	78 ± 2	79 ± 2	78 ± 2
Infiltration density (g cm^3)	17.1 ± 0.2	17.2 ± 0.2	17.1 ± 0.2

Also, the SEM micrographs of fracture surfaces of specimens are shown in Fig. 3. Dark and bright regions present Cu and W phases, respectively. These micrographs are taken to investigate the fracture mode as well as distribution of infiltrated Cu in the samples. As illustrated, the distribution of copper in three prepared composites is uniform. Also, fracture of studied W-Cu composites starts by separation of W-W interfaces and develops by producing cleaved tungsten grain (trans-granular fracture) after strain hardening the matrix and then matrix rupture occurs. Failure of the strain hardened matrix around the tungsten particles cause a large dimple. Also, it can be said that crack formation in these composites starts principally through W-W interface rather than through interface between W grain and the matrix phase [14,26]. It causes brittle behavior of W-Cu composites prepared by infiltration method.

Fig. 4 shows the column plot of relative surface profile loss (surface profile change divided by the initial surface profile of the specimen) after erosion for all three studied materials. As illustrated, specimens fabricated by activator exhibit lower erosion loss compare to specimen without additive. On the other hand, lowest erosion loss belongs to NW (specimen containing Ni additive). It can be said that, addition of sintering activator has a positive effect on the erosion behavior of infiltrated W-Cu composite. As expected, material with higher density (17.4 g·cm^{-3}) showed much less erosion which could be attributed to the higher strength of base tungsten skeleton. Decrease in the strength of tungsten skeleton lead to more damage of sample. At elevated temperature, due to melting or evaporation of Cu phase, the strength of composite is equal to only strength of tungsten skeleton. It was found that at temperatures above 700 °C, the effect of Cu phase on the strength of composite is negligible. In this condition, the strength of skeleton is directly proportional to its density. However, the only density cannot be key parameter in determining the erosion behavior of infiltrated composite. It can be seen in comparing erosion results of CW and PW specimens. In other words, despite to same density of CW and PW specimens, these samples showed different erosion resistance. Then, it is necessary to establish a reasonable relation between microstructure features and erosion behavior of materials.

Fig. 5 shows the optical micrographs form surface morphologies of three samples after erosion test. As illustrated, when the erosion carried out, the surface morphology of eroded samples shows obvious erosion pits and irregular protrusions. These irregular protrusions may be consisting of eroding debris, chips, removed tungsten particles and liquid alumina particles solidified on the surface which orientated in direction of gas stream. Also, the micrographs of the eroded surface in Fig. 6 show inter-granular fracture of the tungsten skeleton (Fig. 6b). The feature observed at this test condition is typical of erosion debris and deposited alumina particles that almost cover the entire surface of sample. As seen from the microstructural features of surface after erosion, it can be concluded that the typical brittle mechanism of inter-granular fracture of tungsten particles (Fig. 6b). On the other hand, erosion pits formed by the loss of grains due to inter-granular cracking or chipping. Based on Gant et al. [28], Brittle materials exhibit an erosive wear mainly due to the chipping. The material removal occurs with the formation of fractures [11,12,28,29]. The erosive particles remove material by chip formation, essentially scraping material off the surface of the solid in a manner similar to machining [29]. Material loss in particle erosion of brittle materials (such as infiltrated W-Cu composites) occurs predominantly through the formation and interaction of a subsurface micro-crack network. In order for these cracks to develop, the