Preparation and properties of W(Al) alloy powders

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Abstract. In order to improve the density and penetrating ability of Al/Ni energetic structural materials, W with the high density and hardness generally was introduced. But the oxidation reaction of W factually is difficult to induce because of the strong binding energy. It then results in the great reduce of energy release. In this work, W(Al) super-saturated solid solution powders with the average particle size of 3.9μm, were synthesized by mechanical alloying. In this super-saturated solid solution, Al atoms are evenly distributed in the W lattice and Al content can reach 80 at.% and 80 at.% Moreover, Al is still stable in the lattice of W but not form Al-W intermetallic, when W(Al) powders were annealed at 1200°C for 30 min in vacuum. As a large amount of Al atoms into W, the activity of W is greatly improved, thus the combustion heat of W(Al) super-saturated solid solution powders can reach about 11.3KJ/g.

1. Introduction

Energetic structural materials (ESMs) refers to a class of energetic materials that have high stability under common conditions, but can produce combustion or even explosion reactions during high-speed impact, releasing a large amount of energy and having high mechanical properties. By taking advantage of the structural and energy integration of ESMs, ESMs with a certain strength can be used to replace the inert parts of existing warheads, such as shards, pill covers, and shells. The damage element formed by the energetic structure material not only has the killing effect of the traditional inert damage element, but also can cause chemical reactions between the components of the material and between the components and the environment after interacting with the target. Generating high temperature and overpressure inside the target will produce greater damage power than traditional warheads, which is an effective way to greatly increase the damage power without increasing the weight of the warhead.

There are three main types of energetic structural materials: metal + metal oxide type (also known as aluminizing agent type), metal + halogen polymer type, and metal type. Metal-based energetic structural materials are composed of metal elements that are susceptible to oxidative combustion and have high combustion heat values. Common Al / Ni [5] metal-based energetic structural materials have high energy density and good energy release characteristics, but their low density, limited penetration ability, and low strength limit its application. At present, adding high-density components
such as W to increase the density of Al / Ni energetic structural materials [6] [7] and enhance its penetration ability. The energy released by metallic energetic structural materials mainly comes from the oxidative and exothermic reaction of the debris cloud and oxygen in the air generated when the material interacts with the target, but the W particles added in Al / Ni are difficult to participate in the oxidative reaction to release energy, so W It is generally considered to be an inert body. Although the addition of W increases the density of the material, it greatly reduces the energy density of the material.

Al has a high heat of combustion (31.1 kJ/g) and is susceptible to oxidative and exothermic reactions with oxygen in the air. Al is currently the most commonly used component in energetic structural materials. From the binary phase diagram of Al-W, it is known that the solid solubility of Al in W under equilibrium state is very small, only 13at.% [8], but the method of mechanical alloying (MA) can greatly improve The solid solubility of Al in W in equilibrium [9]. The introduction of a large number of Al atoms into W is expected to regulate the activity of inert W through Al, making it more likely to interact with oxygen in the air to produce an oxidative exothermic reaction. If W can be burned in the air by modification, then the Al / Ni / W energetic structural material added with modified W will have the characteristics of high specific gravity and high energy density at the same time.

Therefore, this paper attempts to use the method of mechanical alloying to combine Al with W to form W (Al) alloy powder. The introduction of a large amount of Al atoms in W is used to control the combustion characteristics of W. The Al content is 80at.% W (Al) Preparation process and basic properties of alloy powder.

2. Experimental

Mechanical alloying equipment uses Changsha Miqi Instrument Equipment Co., Ltd. YXQM-4L planetary ball mill. The ball mill tank is a 500ml stainless steel ball mill tank. The mill balls are stainless steel balls of different diameters (3 ~ 10mm) mixed at a certain ratio. In the experiment, aluminum powder (5-6 μm, 99.5 wt.%) And tungsten powder (1 μm, 99.8 wt.%) Were used as raw materials.

The Siemens Siemens D-500 X-ray diffractometer was used for phase identification and analysis of the samples; the JSM-6490LV scanning electron microscope was used to observe the surface morphology of the powder particles, and the elemental composition and distribution in different regions were studied; the Germany Netstal STA449F3 DSC performs thermal analysis on W (Al) alloy powder to study its high temperature thermal stability; Thermo Scientific iCAP 7000 type ICP is used to determine element content; Dandong BT-9300Z laser particle size analyzer is used to analyze the average powder particle size; WZR-1TC type oxygen bomb calorimeter measures the combustion heat of powder.

2.1. Preparation of W (Al) alloy powder

Mechanical alloying [10], also known as high-energy ball milling, provides local and instantaneous energy to the reaction system by means of collisions and friction between high-speed moving balls or
between balls and cans, so that different powders repeatedly undergo plastic deformation and cold welding. And fragmentation, diffusion and solid-phase reactions occur between different components to achieve the embedding of atoms and alloying at the atomic level. In the process of mechanical alloying, the driving force for the reaction and phase change is determined by the energy input during the ball milling process. The composition, structure, and properties of the final powder product are affected by many process parameters. Among them, the ball milling time, ball-to-material ratio, etc. Therefore, this paper focuses on the effects of ball milling time and ball-to-material ratio on the formation process of 80at.% Aluminum content W (Al) alloy powder.

(1) Effect of ball milling time

Figure 2.1 shows the XRD patterns of W-80at.% Al mixed powder at different ball milling stages. It can be seen from the Figure that the diffraction peaks of Al and W exist simultaneously before the ball milling begins; as the ball milling time increases, the intensity of the diffraction peaks of Al gradually decreases, indicating that Al is gradually dissolved into the W lattice. Diffraction peaks disappear completely, and finally a W (Al) single-phase solid solution is formed.

In the process of high-energy ball milling, aluminum powder is first extruded into a flake because of its good deformation ability, and brittle tungsten powder is difficult to deform. Under the impact of the grinding ball, the tungsten powder will be hit or pressed into In aluminum flakes, W-Al composite powder is formed. After deformation to a certain extent, the composite powder undergoes work hardening, which results in fragmentation. Welding and fragmentation are repeated. Finally, equilibrium is achieved to obtain W (Al) alloy powder. Figure 2.2 is a scanning electron microscope image of the W-80at.% Al mixed powder after different ball milling times of 0h, 5h, 25h, and 80h. The original mixed powder Al powder is 5-6 μm spherical particles, and W powder is flocculent particles of about 1 μm. In the initial stage of ball milling, the Al powder was extruded into flakes, and W particles were embedded in the inside. After ball milling at 25h, Al powder and W powder were welded together. The degree of welding between the powders was greater than the degree of ball milling crushing, and the composite powder was formed into agglomerated particles. With the further extension of the ball milling time, the lumped powder particles that are welded together undergo severe plastic deformation. Due to work hardening, they are more easily broken, and eventually form alloy powders with a more uniform particle size distribution.

Figure 2.1 XRD patterns of W-80at.% Al powders MA-ed with various time.
Figure 2.2 Microstructures of W-80at.%Al powders MA-ed at various time (a)0h、(b)5h、(c)25h、(d)80h.

Figure 2.3 XRD patterns of W-80at.% Al powders MA-ed with different ball-powder ratio. (2) the effect of ball-to-material ratio
In the process of mechanical alloying, the ball-to-material ratio increases, the number of collisions between the grinding ball and the abrasive increases in a unit time, and more energy is transferred to the powder particles, which accelerates the alloying. Al) Influence of solid solution alloy powder formation process. Figure 2.3 is the XRD spectrum of W-80at.% Al mixed powder at the end of ball milling with different ball-to-material ratios of 10: 1, 15: 1, 20: 1 and 30: 1. It can be seen from the Figure that when the ball-to-batch ratio is 10: 1, the diffraction peaks of Al still exist after the mixed powder with an Al content of 80at.% After 135h ball milling, indicating that Al is not completely dissolved in W; When the ratio is increased to 15: 1, Al is completely solid-dissolved after 135 h of ball milling; while when the ball-to-material ratio continues to increase to 20: 1 and 30: 1, the alloying speed increases rapidly, and the ball milling time required for Al to be completely solid-dissolved into W is For 80h and 70h, the ball milling time is greatly shortened, but when the ball ratio is too high, the powder content is too small and the powder output is too low.

The mechanical alloying process is performed with stainless steel balls and stainless steel tanks, and Fe impurities are inevitably introduced during the ball milling process. Table 1 shows the results of ICP analysis of the Fe content of impurities in W-80at.% Al alloy powder obtained at different ball-to-ball ratios. From the table, it can be seen that the ball-to-ball ratio is small, the ball milling time is long, the ball milling efficiency is low, and the Fe impurity content High; the ball-to-material ratio of 30: 1 has the highest ball milling efficiency, but the extraction rate is too low, but the Fe impurity content is also high, the ball-to-material ratio of 20: 1 is the lowest impurity Fe content. Therefore, comprehensive analysis shows that when the saturated W (Al) solid solution alloy powder with an Al content of 80 at.% Is prepared, 20: 1 is the better ball-to-material ratio.

| ball-powder ratio | milling time | Fe content wt.% |
|-------------------|--------------|-----------------|
| 10:1              | 135h         | 1.851           |
| 15:1              | 135h         | 2.571           |
| 20:1              | 80h          | 0.179           |
| 30:1              | 70h          | 0.386           |

2.2. Properties of W (Al) over saturated solid solution alloy powder
The mechanical alloying method was successfully used to prepare W (Al) over saturated solid solution alloy powder with an Al content of 80 at.% The particle size distribution, thermal stability and combustion characteristics of the alloy powder were also studied in this paper.

(1) Particle size distribution
Figure 2.4 is the cumulative particle size distribution of the obtained W (Al) over saturated solid solution alloy powder with an Al content of 80 at.% It can be seen from the Figure that the particle size distribution of the obtained W (Al) exceeds the saturated solid solution alloy powder is not
constant. Uniform, with a distribution range of 0.1 μm to 75 μm, and an average particle size of about 3.9 μm, which is larger than the original W powder and smaller than the original Al powder.

![Figure 2.4](image)

Figure 2.4 Particle size distribution of W-80at.%Al alloy powders.

(2) Thermal stability

According to the theory of polycrystalline growth, the supersaturated solid solution prepared by large plastic deformation is in an unbalanced state. At a certain temperature, even at normal temperature, processes such as recovery, dissolution and precipitation, and grain growth may change to metastable state. Or steady state. However, recent studies have found that it has a certain thermal stability, and its phase decomposition and grain growth temperature is usually higher. For example, when the temperature is below 400 °C, the microstructure of Cu-Nb supersaturated solid solution prepared by mechanical alloying can remain stable and the second phase precipitation begins to occur at 500 °C [11].

Figure 2.5 is the DSC spectrum of W-80at.% Al powder obtained by ball milling at different times heated to 1200 °C in Ar environment, and Figure 2.6 is the XRD of different types of W-80at.% Al powder in Ar gas after holding at 1200 °C for 30min. Atlas. It can be seen from the Figure that the DSC of the W-80at.% Al mixed powder without ball milling has an exothermic peak and an exothermic peak. The endothermic peak temperature is about 660 °C, which is the endothermic peak of Al melting. The position of the exothermic peak and the endothermic peak is very close, and the temperature is about 670 °C. It is an exothermic peak that the molten Al reacts quickly with the W powder, and the reaction product is Al4W. After 20h ball milling, the melting peaks of Al and the reaction peaks of Al and W are reduced. This is because with the increase of the ball milling time, Al is gradually dissolved into W, and the elemental aluminum powder present in the mixed powder is reduced. After 80h ball milling, Al was completely solid-dissolved into W, and the endothermic and exothermic peaks disappeared, and there was no exothermic phase change exothermic peak that precipitated during the heating process after Al was solid-dissolved. XRD diffraction results show that the W (Al) supersaturated solid solution alloy powder with an Al content of 80 at.% Obtained after ball milling has no other diffraction peaks in the diffraction peaks after holding at 1200 °C in an Ar gas environment, and still maintains a single-phase BCC. The structure is consistent with the diffraction peak of the W (Al) alloy powder before heat treatment, which shows that the obtained 80at.% Al content W (Al) exceeds the saturated solid solution alloy powder can exist stably at 1200 °C and has good high temperature stability.
(3) Combustion characteristics

The particle size of the W powder used in the experiment is 1 μm, and it can stably exist in the air at normal temperature. In the experiment, the combustion heat of the original W powder and the obtained 80at.% Al content W (Al) alloy powder was tested by an oxygen bomb calorimeter. The original W powder was difficult to ignite, and the 80at.% Al content W (Al) alloy powder was easy to ignite. Burning. The actual combustion heat and theoretical combustion heat of W (Al) alloy powder are shown in Table 2. From Table 2, it can be seen that the actual combustion heat of W (Al) alloy powder with 80at.% Al content is 11.3 KJ / g, which is about 78.5% of theoretical heat of combustion. The average particle size of W (Al) with 80at.% Al over the saturated solid solution alloy powder obtained by experiments is about 3.9μm, and W (Al) with particle size less than 1μm accounts for about 26%, so there should be a large number of particle diameters during the test W (Al) alloy
powder larger than 1 μm participates in combustion. This shows that a large amount of Al is solid-dissolved in W, which can improve the W activity, and it is expected that the inert component W in the energetic structural material will be burned. The actual test burning heat value of W (Al) alloy powder is lower than the theoretical heating value, which may be related to that some powders have been oxidized before testing and some super-large particles are not burning during testing.

Table 2. Combustion heat of W-80at.%Al alloy powders.

|       | Al     | W      | W-80at.%Al | W(Al) |
|-------|--------|--------|------------|-------|
| Heat  | 31.1KJ/g | 4.6KJ/g | 14.4 KJ/g | 11.3 KJ/g |

3. Conclusions
In this paper, a large amount of Al atoms are solid-dissolved into W by mechanical alloying, and W (Al) powder with an Al content of 80 at.% Over saturated solid solution alloy is obtained. The average particle size of the powder is about 3.9 μm, and it has good thermal stability. The single-phase BCC structure is still maintained after holding at 1200 °C for 30 minutes in a vacuum. The introduction of a large number of Al atoms improves the activity of W. The obtained W (Al) exceeds the saturated solid solution alloy powder, which is easy to burn and exotherm, and the heat of combustion is 11.3 KJ / g.

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