Effects of glycerol and propylene glycol on the release of volatile substances from electromagnetic pyrolysis of reconstituted tobacco

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Abstract. Compared to traditional combustible cigarettes, heat-not-burn cigarettes can mitigate the production of harmful substances resulting from tobacco combustion, reducing the impact on the surrounding environment. Glycerol and propylene glycol are crucial constituents of the aerosolizer in the thermal decomposition process of tobacco. To investigate the influence of glycerol and propylene glycol additives on the release characteristics of volatile compounds during tobacco electromagnetic heating, experiments were conducted using tobacco materials with varying proportions of glycerol and propylene glycol, along with different metal powder additives, under varying voltage conditions. The results indicate that, with an increase in propylene glycol content in tobacco, tobacco samples with added nickel powder exhibited a higher release of volatile compounds compared to those with added iron powder. When nickel powder was used as the electromagnetic heating metal powder, an increase in propylene glycol content initially led to suppression and subsequently enhancement of thermal decomposition in the reconstituted tobacco. In contrast, when iron powder served as the electromagnetic heating metal powder, an increase in propylene glycol content initially promoted and later inhibited thermal decomposition in the reconstituted tobacco. These findings provide valuable insights for the development of future tobacco electromagnetic heating processes, aiding in the reduction of the environmental impact of traditional cigarette combustion products in the future.

Keywords: Electromagnetic heating, Pyrolysis, Glycerol.

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Conventional combustible cigarettes release a substantial amount of harmful substances, such as polycyclic aromatic hydrocarbons, into the environment during use, significantly impacting the physical well-being of non-smokers. Heat-not-burn cigarettes, due to their lower operating temperatures, emit over 90% fewer harmful substances compared to traditional cigarettes, garnering widespread attention [1-3].

Presently, the heating source for heat-not-burn cigarettes predominantly employs metal resistance to heat the tobacco stick, which presents issues such as slow heating rates and uneven release of volatiles. Electromagnetic heating technology offers advantages, including precise temperature control, rapid heating rates, high energy efficiency, and reduced environmental impact. It holds the potential to effectively address the challenges posed by metal resistance heating, making it a promising alternative for heating in heat-not-burn cigarettes [4-6].

Aerosolizing agents play a pivotal role as additives in heat-not-burn cigarettes, facilitating the release of nicotine and flavor compounds during the thermal decomposition of tobacco.10-14 Glycerol and propylene glycol are crucial constituents of aerosolizing agents, and their composition ratios significantly influence the release characteristics of volatile compounds during the thermal decomposition of heat-not-burn cigarettes. Therefore, against the backdrop of heat-not-burn cigarettes, this study delves into the intricate relationship between aerosolizing agent composition and electromagnetic heating. Specifically, it examines the impact of varying proportions of glycerol and propylene glycol, in conjunction with different metal powder additives, on the release of volatile substances during electromagnetic pyrolysis.

2 Materials and Methods

2.1 Electromagnetic pyrolysis of reconstituted tobacco

The specialized reconstituted tobacco samples with different types of aerosolizing agents were provided by Hubei Xinye Reconstituted Tobacco Development Co., Ltd. The gases and chemicals used in the experiments included nitrogen (purity > 99.999%, supplied by Wuhan Huaerwen Industrial Co., Ltd.), helium (purity > 99.999%, supplied by Wuhan Huaerwen Industrial Co., Ltd.), dichloromethane (chromatography grade, Aladdin), methanol (chromatography grade, Aladdin), and tetrahydrofuran (chromatography grade, Aladdin).

Electromagnetic pyrolysis experiments involving reconstituted tobacco leaves with various aerosolizing agents were conducted in a specially designed fixed-bed quartz reactor, as depicted in Figure 1. The internal diameter of the reactor was 8 mm. The heating coil parameters were as follows: height of 20 mm, diameter of 10 mm, and a total of 8 turns. The samples of reconstituted tobacco leaves were placed on a sieve plate within the reactor, ensuring they were entirely within the heating range of the coil. During the pyrolysis process, carrier gas flowed in from above the samples, carrying volatile compounds generated during the pyrolysis of reconstituted tobacco leaves and exiting from below, where they were subsequently condensed and collected. High-purity nitrogen gas was employed as the carrier gas for the pyrolysis process, with a flow rate of 50 $mL \cdot min^{-1}$. The oil yield (%) represented the percentage of the mass of condensed oil after the pyrolysis of reconstituted tobacco leaves relative to the total sample mass, while the char yield (%) denoted the percentage of char mass after the pyrolysis of reconstituted tobacco leaves relative to the total sample mass.

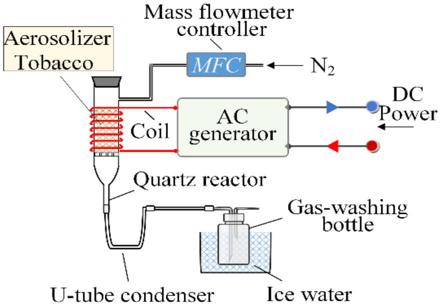

Fig. 1. Schematic diagram of the electromagnetic heating device.

2.2 Product analysis

Gel permeation chromatography (GPC) with an Agilent 1260II instrument was used to detect the molecular weight distribution of the pyrolysis oils. The gel column used was an OligoPore with dimensions of 7.5×300 mm. A refractive index detector was employed for detection. The mobile phase consisted of chromatography-grade tetrahydrofuran (THF). During the testing process, the column temperature was maintained at 40 °C, and the detector temperature was set at 45 °C, with a mobile phase flow rate of 1 mL·min^{-1}. Before analysis, the column was equilibrated by flushing it with the mobile phase until the baseline fluctuations were within 50 units [7].

Gas chromatography-mass spectrometry (GC-MS) with a Thermo Scientific Trace 1300/ISQ instrument was used to characterize the effective compounds in the pyrolysis oil solution. An HP-INNOWax column (30 m × 0.25 mm × 0.25 mm) was employed for chromatographic separation. High-purity helium gas (purity > 99.999%) was used as the carrier gas with a flow rate of 1 ml·min^{-1}. The liquid injection mode was set to splitless with an injection volume of 1 μL, and the inlet temperature was maintained at 250 °C. The detection results were compared with the National Institute of Standards and Technology (NIST) database (2014 version) for identification [8].

3 Results and discussion

3.1 Effect of propylene glycol ratio on the yield of bio-oil and coke during electromagnetic pyrolysis of reconstituted tobacco

Aerosolizing agents play a crucial role in the production of reconstituted tobacco, significantly influencing the release characteristics of flavor compounds during tobacco pyrolysis. The primary components of these agents are propylene glycol (PG) and glycerol, and to investigate the impact of their composition on the electromagnetic pyrolysis of tobacco, aerosolizing agents with varying ratios of PG and glycerol were prepared.

These agents, along with different metal powders, were added to reconstituted tobacco to create specialized samples. The pyrolysis product yields for various reconstituted tobacco samples at 12 V are presented in Figure 2. The results demonstrate that, overall, the addition of nickel powder to reconstituted tobacco enhances the release of volatile fractions compared to samples without nickel powder. When nickel powder is added, an increase in the proportion of PG in the aerosolizing agent leads to an initial decrease followed by a significant increase in oil yield, accompanied by a corresponding trend in char yield – initially increasing and then decreasing. This suggests that in the presence of nickel powder, a lower proportion of PG inhibits the release of volatile compounds during electromagnetic pyrolysis. Conversely, when the aerosolizing agent contains a higher proportion of PG, it promotes the release of volatile compounds, resulting in a significant increase in oil yield, with the highest enhancement reaching 8.6%.

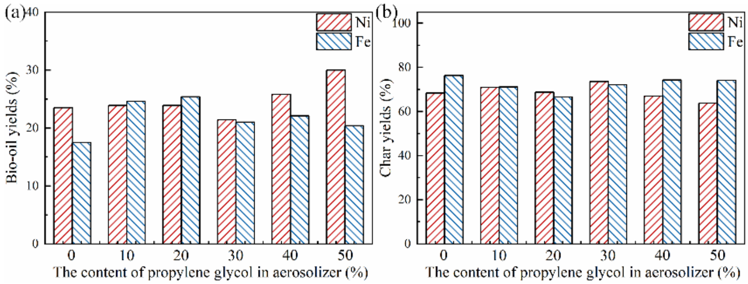

Fig. 2. The pyrolysis products yields of the reconstituted tobacco with different propylene glycol ratios under 12 V.

However, when iron powder is added, an increase in the proportion of PG in the aerosolizing agent initially leads to an increase in oil yield, accompanied by an increase in char yield. This implies that, with iron powder, a lower proportion of PG encourages the release of volatile compounds, resulting in increased oil yield, with the highest improvement reaching 7.9%. Nevertheless, as the proportion of PG in the aerosolizing agent increases, it eventually inhibits the release of volatile compounds, leading to a gradual decrease in oil yield. These findings indicate that the influence of PG proportion in the aerosolizing agent varies significantly with the presence of different metal powders in reconstituted tobacco, suggesting an intricate interplay between the aerosolizing agent and various metal powders, a relationship potentially dependent on the characteristics of the metal powders.

Furthermore, we conducted specialized reconstituted tobacco experiments using different metal powders and the optimized aerosolizing agent ratio to investigate the variation in pyrolysis product yields under different heating voltages (8-12 V), as illustrated in Figure 3. Under the optimal aerosolizing agent ratio, as the heating voltage increased, there was a significant enhancement in oil yield during the pyrolysis of reconstituted tobacco. When nickel powder was added, the oil yield at 12 V was three times higher than at 8 V. This phenomenon can be attributed to the substantial increase in pyrolysis temperature with higher external input voltage, resulting in more thorough pyrolysis and a rapid increase in the release of volatile fractions [9-10]. Comparing reconstituted tobacco samples with added iron powder and those with added nickel powder under different voltages, it was observed that the pyrolysis of reconstituted tobacco with added nickel powder outperformed that with iron powder, and this effect significantly intensified with increasing heating voltage. This indicates that the effects induced by changes in metal type and aerosolizing agent ratio become more pronounced with higher heating voltage. At 12 V voltage, the maximum difference in oil yield between the two cases reached 4.6%, underscoring the substantial influence of electromagnetic heating parameters on aerosolizing agent performance.

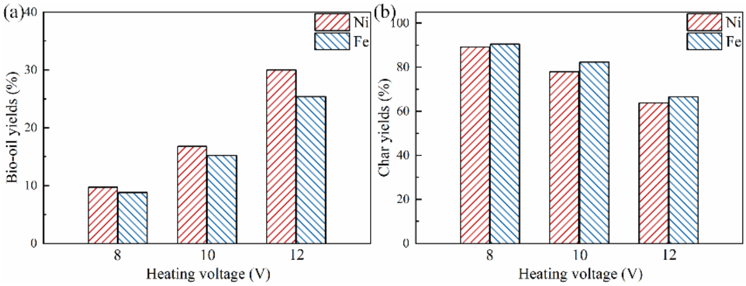

Fig. 3. The pyrolysis products yields of the reconstituted tobacco under different voltages.

3.2 Effect of propylene glycol ratio on molecular weight distribution of bio-oil during electromagnetic pyrolysis of reconstituted tobacco

The condensed oils collected after the pyrolysis of specialized reconstituted tobacco samples with different metal powder types and aerosolizing agent compositions were subjected to molecular weight characterization analysis, as depicted in Figure 4(a). For reconstituted tobacco samples with added nickel powder, as the proportion of propylene glycol in the aerosolizing agent increased, the average molecular weight of the pyrolysis-derived oil exhibited an initial increase followed by a decrease. Generally, as pyrolysis progresses, large organic molecules tend to break down into smaller ones, leading to a significant reduction in the molecular weight of volatile compounds released during pyrolysis [11-15]. This suggests that with the addition of nickel powder, the increasing proportion of propylene glycol in the aerosolizing agent initially inhibits and subsequently promotes the pyrolysis of reconstituted tobacco, resulting in a trend of increasing and then decreasing molecular weight in the collected oil.

Furthermore, when combined with yield information analysis, it becomes evident that for nickel powder, the increase in propylene glycol proportion in the aerosolizing agent first inhibits the pyrolysis of reconstituted tobacco and the release of volatile fractions. During this phase, the oil yield and the content of small molecular aroma compounds in the oil are relatively low. With a further increase in the proportion of propylene glycol in the aerosolizing agent, the pyrolysis of reconstituted tobacco and the release of volatile fractions are promoted, leading to an increase in oil yield and the content of small molecular aroma compounds. In contrast, for reconstituted tobacco with added iron powder, unlike nickel powder, the average molecular weight of the pyrolysis-derived oil exhibits an initial decrease followed by an increase as the proportion of propylene glycol in the aerosolizing agent increases. This indicates that with the addition of iron powder, the increasing proportion of propylene glycol initially promotes and subsequently inhibits the pyrolysis of reconstituted tobacco, resulting in a trend of decreasing and then increasing molecular weight in the collected oil. This observation aligns with the yield information, illustrating that for iron powder, the increase in the proportion of propylene glycol in the aerosolizing agent initially promotes the pyrolysis of reconstituted tobacco and the release of volatile fractions. During this phase, the oil yield and the content of small molecular aroma compounds in the oil are relatively high. With a further increase in the proportion of propylene glycol in the aerosolizing agent, the pyrolysis of reconstituted tobacco and the release of volatile fractions are inhibited, leading to a gradual reduction in oil yield and the content of small molecular aroma compounds.

Furthermore, the molecular weight distribution patterns of the pyrolysis oils from specialized reconstituted tobacco samples with different metal powders and the optimal aerosolizing agent proportion under various voltages were investigated in more detail, as illustrated in Figure 4(b). The results indicate that the molecular weight distribution patterns of the pyrolysis oils from specialized reconstituted tobacco samples with different metal powders and the optimal aerosolizing agent proportion under different voltages are essentially similar. As the heating voltage decreases, the average molecular weight of the pyrolysis-derived oil gradually decreases, indicating that the reduction in heating voltage significantly inhibits the pyrolysis process, leading to a substantial increase in molecular weight in the oil. The aforementioned yield results suggest that as the heating voltage increases from 8 V to 12 V, the yield of collected oil significantly increases. Combined with the molecular weight distribution analysis, it is evident that an increase in heating voltage leads to the release of small molecular additives, moisture, and effective components from the pyrolysis, enriching the aroma and flavor in the resulting volatiles.

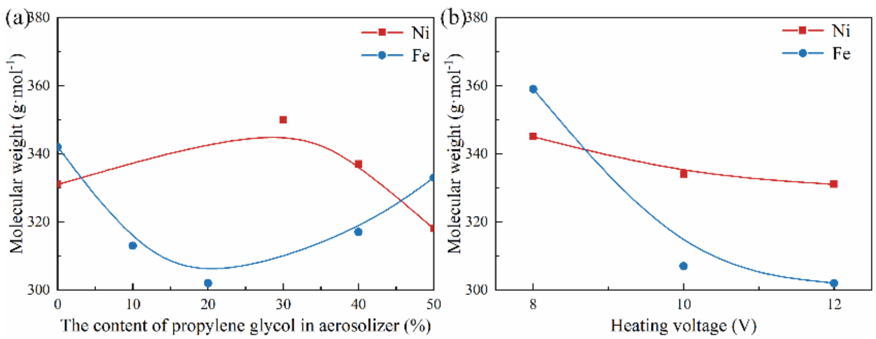

Fig. 4. The molecular weight distribution of the reconstituted tobacco pyrolytic oil with different propylene glycol ratios (a) and different voltages (b).

3.3 Effect of propylene glycol ratio on the distribution of bio-oil component during electromagnetic pyrolysis of reconstituted tobacco

To gain further insight into the distribution of specific components in the oils, gas chromatography-mass spectrometry (GC-MS) analysis was conducted on the pyrolysis oils. The content distribution of typical components in the volatiles is depicted in Figures 5 and 6. For reconstituted tobacco samples containing nickel powder, with an increase in the proportion of propylene glycol in the aerosolizing agent, the proportion of propylene glycol released during pyrolysis also increases. Consequently, the content of propylene glycol in the collected oil significantly rises, while the content of glycerol markedly decreases.

However, the increase in the proportion of propylene glycol in the aerosolizing agent has only a slight promoting effect on the release of nicotine in the pyrolysis oil. This suggests that the variation in aerosolizing agent proportion does not significantly impact the release of the main component, nicotine, during the tobacco pyrolysis process. However, as the proportion of propylene glycol in the aerosolizing agent increases, there is a more pronounced change in aroma compounds in the pyrolysis oil, including acids, esters, and olefins, as shown in Figure 5(b).

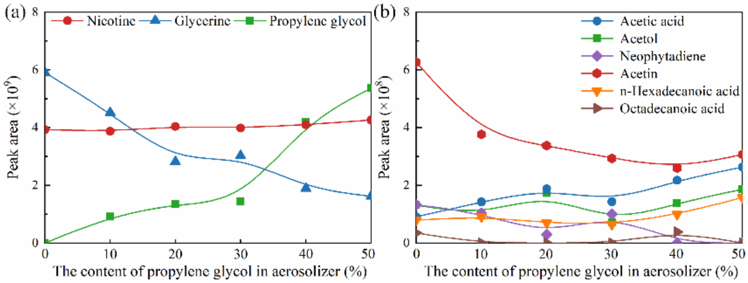

Fig. 5. The peak areas of the species in reconstituted tobacco pyrolytic oil detected by GC-MS with nickel powders and different propylene glycol ratios under 12 V.

With an increase in the proportion of propylene glycol in the aerosolizing agent, the first notable change is the significant decrease in the content of acetin, which is attributed to the marked reduction in glycerol content in the aerosolizing agent. This decrease inhibits the esterification reaction between acetic acid and glycerol, resulting in a rapid decline in acetin content. Correspondingly, the main component, acetic acid, in the pyrolysis oil significantly increases. Furthermore, as the proportion of propylene glycol in the aerosolizing agent increases, the content of acetol and n-hexadecanoic acid in the oil gradually rises, indicating that propylene glycol promotes the release of these small-molecule acids and alcohols. However, for neophytadiene, an olefinic compound, an increase in the proportion of propylene glycol has a rapid inhibitory effect on its content, indicating that propylene glycol has a certain inhibitory effect on the release of olefinic aroma compounds.

For reconstituted tobacco samples containing iron powder, as shown in Figure 6, with an increase in the proportion of propylene glycol in the aerosolizing agent, the proportion of glycol released during pyrolysis also increases. Consequently, the content of glycol in the collected oil significantly rises. However, in contrast to reconstituted tobacco samples containing nickel powder, an increase in the proportion of propylene glycol initially promotes the release of glycerol in the tobacco, followed by a rapid increase in the proportion of propylene glycol, leading to a decrease in glycerol release. This indicates that for reconstituted tobacco samples containing iron powder, a slight increase in the proportion of propylene glycol promotes glycerol release.

Furthermore, with an increase in the proportion of propylene glycol in the aerosolizing agent, the nicotine content in the pyrolysis oil initially remains stable and then rapidly decreases. This suggests that a minor addition of propylene glycol has no significant impact on the release of nicotine in the pyrolysis of reconstituted tobacco containing iron powder, but significant inhibition of nicotine release occurs with a larger proportion of propylene glycol.

Simultaneously, with an increase in the proportion of propylene glycol in the aerosolizing agent, there is a more noticeable change in aroma compounds in the pyrolysis oil, including esters and olefins, as depicted in Figure 6(b). As the proportion of propylene glycol initially promotes the release of glycerol in tobacco, it enhances the esterification reaction between acetic acid and glycerol, resulting in a significant increase in acetin content. Subsequently, as glycerol release from tobacco diminishes, the content of acetin significantly decreases. Similar to reconstituted tobacco samples containing nickel powder, with an increase in the proportion of propylene glycol, the content of neophytadiene, an olefinic rapidly decreases, indicating that propylene glycol has an inhibitory effect on the release of olefinic compounds.

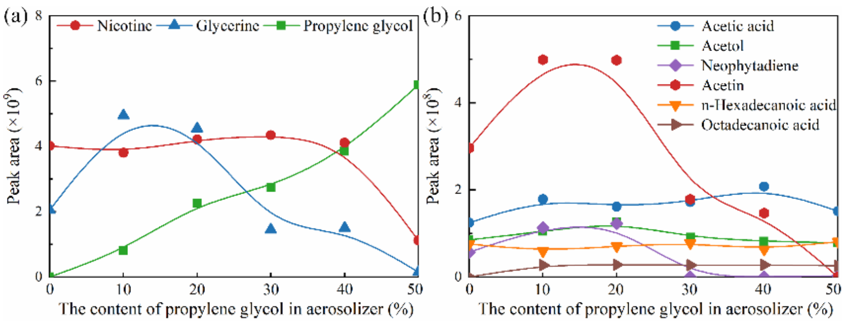

Fig. 6. The peak areas of the species in reconstituted tobacco pyrolytic oil detected by GC-MS with iron powders and different propylene glycol ratios under 12 V.

However, changes in the proportion of propylene glycol in the aerosolizing agent have a relatively minor impact on acid compounds in the oil, such as n-hexadecanoic acid and octadecanoic. This further underscores the presence of interactions between the aerosolizing agent and different metal powders, with the nature of these interactions being associated with the characteristics of the metal powders.

Further investigation into the distribution of specific components in the pyrolysis oil from different reconstituted tobacco samples under varying heating voltages is presented in Figure 7. It is evident that as the heating voltage increases, regardless of the presence of different metal powders and aerosolizing agents, there is an overall upward trend in the content of major components such as nicotine, glycerol, and propylene glycol, as well as key flavor compounds like n-hexadecanoic acid, octadecanoic, and neophytadiene. These findings align closely with the results obtained for yields and molecular weight distribution, indicating that the elevation in heating voltage not only facilitates the release of aerosolizing agents and nicotine but also further promotes the release of aroma compounds from the reconstituted tobacco, enhancing the flavor profile of the emitted volatiles.

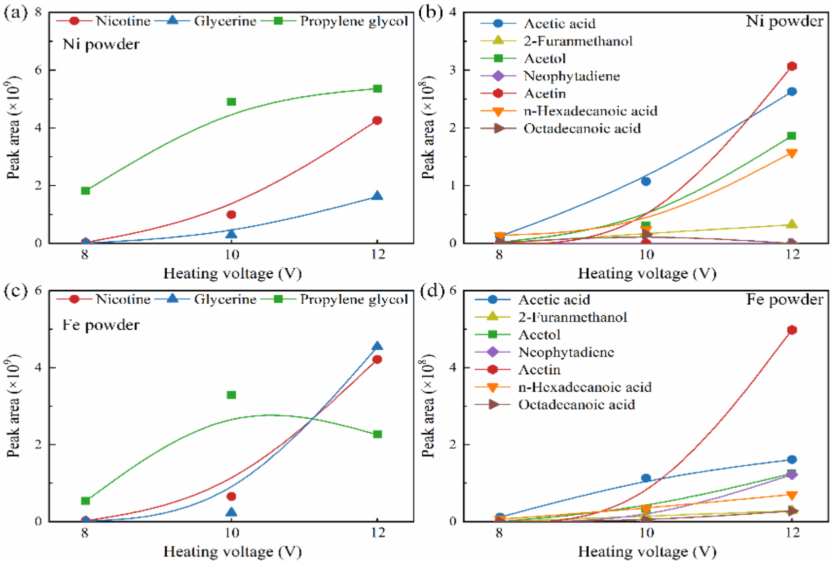

Fig. 7. The peak areas of the species in reconstituted tobacco pyrolytic oil detected by GC-MS with different metal powder types under different voltages.

4 Conclusions

To investigate the impact of glycerol and propylene glycol addition on the release characteristics of volatile compounds during tobacco electromagnetic pyrolysis, experiments were conducted on tobacco materials containing varying ratios of glycerol and propylene glycol, along with different metal powders, under different voltage conditions. In the case of reconstituted tobacco samples containing nickel powder, an increase in the proportion of propylene glycol within the aerosolizing agent initially inhibits the pyrolysis of reconstituted tobacco and the release of its volatile components. This leads to a reduction in oil yield and a suppression of the release of small-molecule flavor compounds. However, a further increase in the proportion of propylene glycol in the aerosolizing agent, promotes the pyrolysis of reconstituted tobacco and the release of its volatile components, resulting in an increase in oil yield and the enhanced release of small-molecule flavor compounds. Conversely, for reconstituted tobacco containing iron powder, an increase in the proportion of propylene glycol initially stimulates the pyrolysis of reconstituted tobacco. However, as the proportion of propylene glycol in the aerosolizing agent increases further, it exhibits an inhibitory effect on the pyrolysis of reconstituted tobacco. These findings underscore the intricate interactions between aerosolizing agents and different metal powders and their dependence on the specific characteristics of the metal powders employed.

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