Design of the thixotropic lubricant and its influence on compaction behavior of Cr-alloyed PM steel

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A multifunctional lubricant containing thixotropic components was designed for Cr-alloyed PM steel. The thixotropic properties of the lubricant components, compaction behavior of the powder mixture and the lubrication effects of the lubricant were explored. The results demonstrate that the thixotropic components in the lubricant are polyethylene wax and polyamide wax. When the compaction pressure increases from 400 MPa to 800 MPa, the polyamide wax content corresponding to the maximum green density increases from 0% to 30%. The thixotropic properties of polyethylene wax and polyamide wax are reflected at low and high pressures, respectively. By the application of new lubricant in binder treatment technology, alloying additives are effectively filled into the pits of iron particles, the apparent density, flowability and compressibility of mixture are much higher than those of other lubrications. When the content of both polyamide wax and polyethylene wax was 20%, the apparent density and flowability reached 3.46 g/cm^3 and 34.88 s/50 g, respectively. And the green density of compacts reached 7.18 g/cm^3 at 600 MPa and 7.37 g/cm^3 at 800 MPa.

1. Introduction

The introduction of Cu, Ni, Mo and other alloy elements in iron-based powder metallurgy products can effectively improve mechanical properties [1,2]. In recent years, due to the volatility in prices of Cu and Ni in the international market and recent regulations limiting the use of Ni and environmental problems caused by Cu-containing parts, searching for new alloying elements to replace has been a hotspot. The earliest approach to introducing more cost-effective PM alloys was the development of pre-alloyed Cr-containing grades, first introduced in 1990s. As the most common alloying element in heat-treated steel, Cr can improve the corrosion resistance of parts. Mn is well received with its highest multiplying effect in terms of hardenability and low price. Therefore, replacing Cu and Ni in alloy composition with a certain amount of Cr and Mn can reduce the cost and maintain excellent mechanical properties at the same time.

Compared with Cu and Ni, the addition of Cr and Mn alloy powder will further reduce the compressibility of premixed powder caused by their high hardness. Adding lubricants to raw powder can reduce the pressure loss caused by friction between die wall and powder, powder and powder during compaction processes, and improve the compressibility of powder [3–5]. Nevertheless, the addition of lubricants also has disadvantages, the binding force between metal powders in compacts decreases due to the barrier of lubricants, which reduces the strength of compacts [6]. Moreover, traditional lubricants (such as zinc stearate, lithium stearate, etc.) usually leave harmful metal or metal oxide residues in sintering parts and sintering furnaces, affecting product quality and production efficiency.

In addition to compressibility, the introduction way of alloying elements is more important for PM products. The widespread method of introducing alloy elements in production is to add quantitative element powder or alloy powder according to the target alloy composition. However, owing to the different morphology, particle size and specific gravity of the powders, the resulting powder mixtures are susceptible to segregation during mixing or handling, which leads to compositional variations [7,8]. There are basically two main routes to reduce the composition segregation, either by the use of completely prealloyed iron

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powder, or by thermal diffusion or using binder to bond alloy powder on the surface of matrix iron particles [9–11]. Whether completely prealloyed or thermal diffusion bonding, will reduce the compaction performance of the mixture more or less and increase the costs [12,13].

In this work, a multifunctional lubricant was designed by adding multiple lubricating and thixotropic components. The relationship between proportion of thixotropic components and compaction behavior of the powder mixture were explored and the lubrication effects of new lubricant and three common lubricants were compared. The alloy powders were uniformly adhered on the surface of iron powder and excellent compressive properties of the mixture were guaranteed at a lower new lubricant content.

2. Materials and experimental procedure

Fe-0.1Mn-1Ni-0.8Mo-1Cr-0.6C cost-effective lean alloyed steel powder was prepared by binder treatment technology. Considering the higher oxygen affinity and more stable oxides of Cr and Mn compared with Cu and Ni, the two elements cannot be added as elemental powder and need to be added in the form of alloys [14]. Fe-Cr and Fe-Mn alloy powder was used instead of pure Cr powder and pure Mn powder in the experiment, respectively. The iron powder used in the experiment was LAP 100.29 water-atomized iron powder (Laiwu Iron&Steel Group Powder Metallurgy Co., LTD) with average particle size of 140 μm. As alloy additives, the particle size of Fe-Mn, Ni, Fe-Mo, Fe-Cr and C is less than 8 μm. EBS and stearic acid are the main lubricating components in the lubricant designed in this experiment. Thixotropic additives include polyethylene wax and polyamide wax and the total content of the lubricant in the mixture is 0.3 wt.%. In order to evaluate the lubrication effect of the new lubricant, EBS, zinc stearate and Superlube 2.0 were selected as the comparison. The equipment for binder treatment technology is double-cone spray mixer. The lubricant is first dissolved in the mixed solution of trichloromethane and n-heptane at 80 °C, and then sprayed into the mixture during mixing process under the high pressure of nitrogen to mix with the powder evenly. The other lubricants for comparing were added to the mixer with alloy additives before mixing and the mixing time was 3 hours, the same as the binder treatment.

The RS6000 rotary rheometer (HAAKE, Germany) was used to analyse the rheological properties of the lubricant components. The shear rate was set to 0.1–100 rad/s and the experimental temperature was 25 °C. The YAW-600G pressure tester was used to prepare compacts under the compaction pressure of 400–800 MPa. For different lubricants, five samples were prepared under each pressure and the density was calculated by mass–volume method. Particle size distribution of the mixture was analyzed by BT-9300H laser particle size analyzer. The distribution of alloying elements of the powder was examined using TESCAN tungsten filament scanning electron microscope (SEM) equipped with EDS system.

3. Results and discussion

3.1. Rheological analysis of lubricant components and its effect on compaction behavior

The purpose of this experiment is to find out the relationship between thixotropic components of lubricant and compaction behavior of the powder. However, it is difficult to capture the change of lubricant state after loading during compaction. The state transition of lubricant can be inferred by analyzing its rheological behavior. Thixotropy describes a reversible change in structure and the relationship among fluid viscosity, shear force and shear rate [15,16]. The structure is destroyed when subjected to external forces, and when the external forces disappear, the structure can gradually recover. Thixotropic properties are usually quantified by thixotropic index and thixotropic-loop method, and the area of thixotropic-loop is positively correlated with thixotropic properties [17]. Figure 1 shows the thixotropic-loops of EBS, stearic acid, polyethylene wax and polyamide wax. With the shear rate increases from 0 rad/s to 100 rad/s and then decreases from 100 rad/s to 0 rad/s, the shear rate variation of four components are completely different. Since the upper and lower curves of stearic acid and EBS substantially coincide, it can be considered that they have no thixotropy. Unlike EBS and stearic acid, the two shear stresses corresponding to polyethylene wax and polyamide wax differ sharply at the same shear rate. Obviously, the thixotropy components in the lubricant are polyethylene wax and polyamide wax. The viscosity of each component is further analyzed as a function of shear rate and shear stress, as shown in Figure 2. The viscosity of all the four components is higher than 10,000 Pa•s with no shear stress (the shear rate is 0 rad/s). With the increase in shear rate, the viscosity of EBS and stearic acid decreases rapidly, while that of polyethylene wax and polyamide wax decreases slightly slowly. When the shear rate increases to 30 rad/s, the viscosity of the components decreases to less than 1000 Pa•s, transformed from solid to liquid. The critical solid–liquid shear rate of polyethylene wax is 5 rad/s, and that of polyamide wax reaches 27 rad/s, higher than the former. As can be seen from the Figure 2(b), the critical solid–liquid shear stresses of polyethylene wax and polyamide wax are 150 MPa and 1500 MPa, respectively, and the latter is ten times of the former.

In order to better determine the effect of thixotropic components on powder compaction behavior, five lubricants with different composition ratios were designed, as shown in Table 1. EBS and stearic acid are commonly used as lubricants in iron-based powder metallurgical products, and the content of the

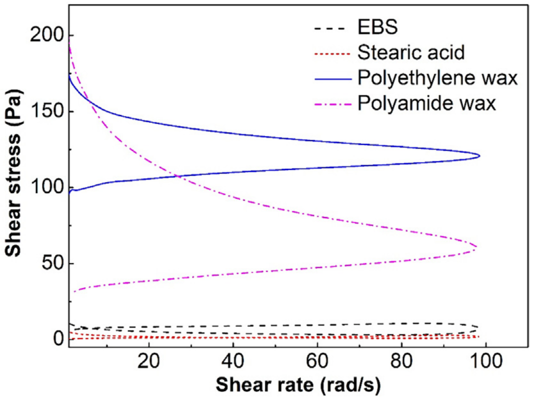

FIGURE 1

The thixotropic-loops of EBS, stearic acid, polyethylene wax and polyamide wax.

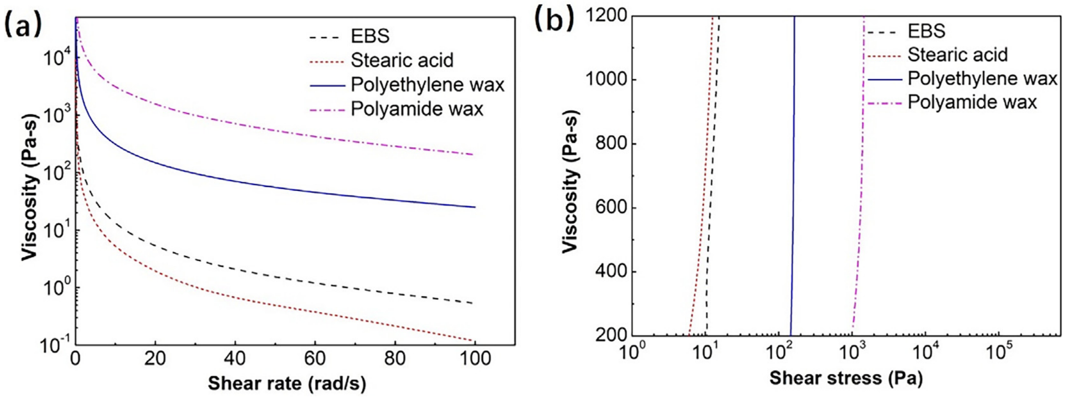

FIGURE 2

The variation of viscosity with shear rate(a) and shear stress(b) of EBS, stearic acid, polyethylene wax and polyamide wax.

TABLE 1

Composition of the lubricants (wt.%).

No.	EBS	Stearic acid	Polyethylene wax	Polyamide wax	other
1#	30%	20%	40%	0%	10%
2#	30%	20%	30%	10%	10%
3#	30%	20%	20%	30%	10%
4#	30%	20%	10%	30%	10%
5#	30%	20%	0%	40%	10%

two is fixed at 50 wt.%. The contents of ferrocene, isooctanoic acid and 168 antioxidants were set at 10% and the total content of thixotropic component polyethylene wax and polyamide wax is 40%. The five kinds of lubricants were separately mixed with powder by a double-cone spray mixer to obtain the binder-treated powder. Figure 3 shows the variation of green density with the content of polyamide wax under the compaction pressure of 400–800 MPa. The content of polyamide wax corresponding to the highest green density under different compaction pressures is different. When the compaction pressure rises from 400 MPa to 800 MPa, the polyamide wax content corresponding to the maximum green density increases from 0% to 30%. Based on the analysis of rheological behavior of polyamide wax and polyethylene wax, it can be concluded that the shear thinning of polyethylene wax under shear stress will occur during the compaction process when the pressing pressure is low, which will reduce the viscosity of the lubricant and enhance the lubrication effect. And with the deformation and friction of the powder particles, the lubricant can be transferred from the surface of the powder to the pore between the particles, thereby further increasing the green density. Therefore, with low content of polyamide wax and high content of polyethylene wax added, higher green compact density can be obtained at low compaction pressure. When polyethylene wax content is 40% and without polyamide wax added, the green density reaches 6.8 g/cm^3 at 400 MPa. However, when the content of polyamide wax is low, a large number of lubricants are transferred to the interstitial pore of particles prematurely with the increase in compaction

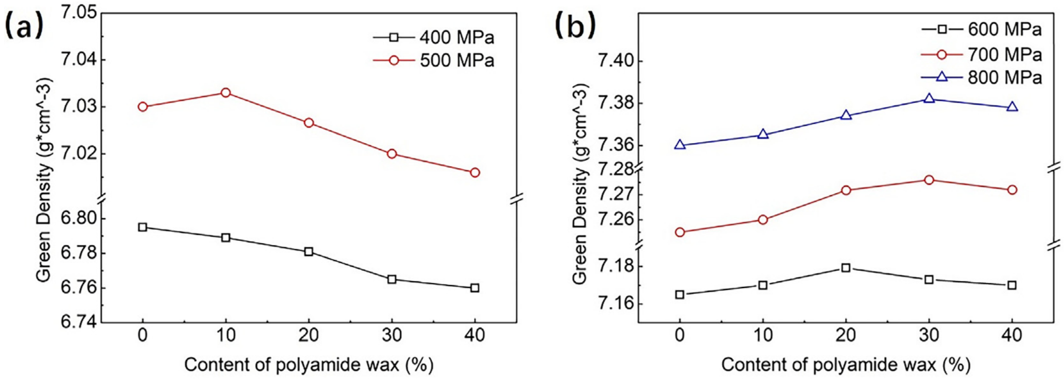

FIGURE 3

The variation of green density with the content of polyamide wax under the compaction pressure of 400–800 MPa.

pressure, so that the effective friction reducing component in the powder is reduced, which is disadvantageous for the increasing in green density. Unlike polyethylene wax, the thixotropic behavior of polyamide wax can only be stimulated at higher compaction pressure and the addition of a certain amount of polyamide wax contributes to the further increase in density under high pressure. Under the pressure of 600 MPa, when the content of both polyamide wax and polyethylene wax was 20%, the compact density is the highest, reaching 7.18 g/cm^3. When the compaction pressure rises above 700 MPa, the friction reducing effect of the lubricant in the first half of the compaction process (low pressure) decreases, so the content of polyamide wax corresponding to the highest green density increases. When the content of polyamide wax is 30%, the green density reaches 7.28 g/cm^3 at 700 MPa and 7.38 g/cm^3 at 800 MPa.

Figure 4 shows the change of the ejection pressure with the polyamide wax content at compaction pressure of 400–800 MPa. Under the compaction pressure of 400 and 500 MPa, when the content of polyamide wax is 0%, the ejection pressure reaches the lowest, which is 12.5 and 13.7 MPa, respectively. With the increase in compaction pressure, the content of polyamide wax corresponding to the minimum ejection pressure increases gradually. The minimum ejection pressure was obtained at polyamide wax content of 10% at 600 MPa, which was 16.9 MPa. When the compaction pressure rises to 700 MPa, the polyamide wax content corresponding to the lowest ejection pressure increases to 20%. The law of ejection pressure changing with the content of polyamide wax can also reflect that the lubrication enhancement of polyamide wax was mainly exhibited in high compaction pressure.

3.2. Comparison of lubrication effect

The lubricant with the highest compact density (20% of polyamide wax and polyethylene wax) under 600 MPa was selected, and the lubricating effect with zinc stearate, Superlube 2.0 and EBS were compared. The content of zinc stearate is 0.75 wt.% and the other lubricants 0.3 wt.%. Figure 5 shows the particle size of the powder with different lubricants added. The particle size distribution of zinc stearate is basically the same as that of EBS, bimodal size distribution of the powder mixture is observed and the intensity of the secondary peaks are equivalent. The particle size corresponding to the secondary peak is 5 μm, which is consistent with the particle size of the alloying additives, indicating that the formation of the secondary peak is caused by the alloy powder not adhering on the surface of the iron particles and EBS and zinc stearate have almost no adhesive attraction during the mixing process. Compared with EBS and zinc stearate, the sub-peak strength of Superlube 2.0 is reduced by about 30%, suggesting that Superlube 2.0 can promote bonding to some extent. With new lubricant added, the secondary peak disappears basically, which manifests that the amount of free alloy powder decreases, and most alloy additives can adhere on the surface of iron particles well. Figure 6 shows the alloy element distribution of the powder with new lubricant added. Alloying additives such as Fe-Mo, FeMn and FeCr powders are filled into pits of iron particles, which enhance the smoothness of iron powder. Due to the small radius of curvature and high energy in the depression, the surface energy of iron powder can be reduced by the fine alloying powder adhering to the pits of iron particle [10]. In addition, the mechanical interlock is easy to form in the depression due to the large contact area between iron particle and alloying additives, and the probability of the fine powder falling off due to collision

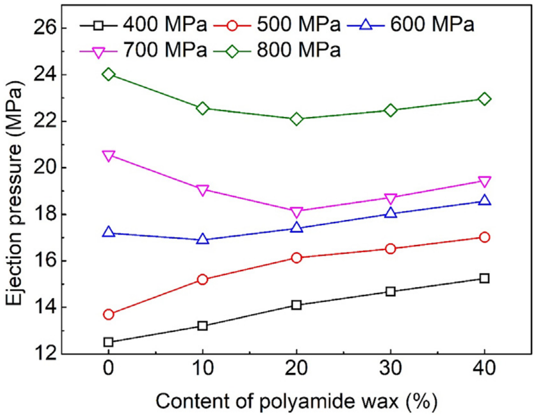

FIGURE 4

Ejection properties over a range of compaction pressures.

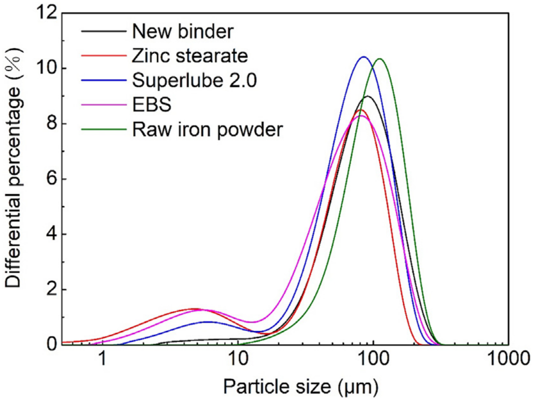

FIGURE 5

Particle size distribution with different lubricants added.

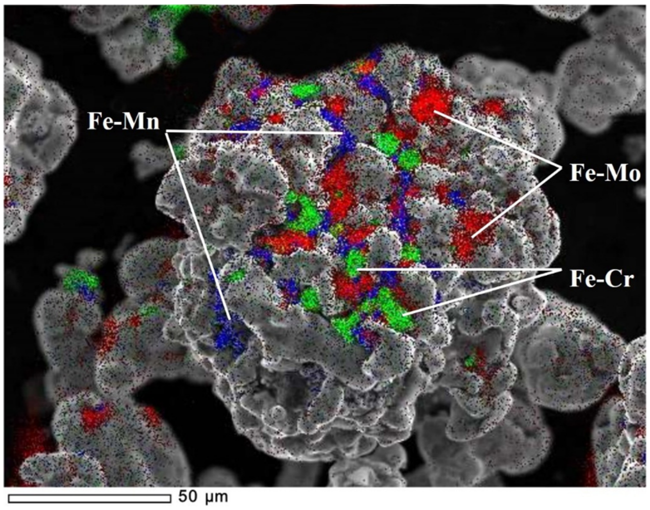

FIGURE 6

Alloy elements distribution of the powder with new lubricants added.

TABLE 2

Powder properties of mixture with different lubricants added.

	Raw iron powder	Premixed powder	Zinc stearate	Superlube 2.0	New lubricant	EBS
Apparent density (g/cm^3)	3.09	3.15	3.18	3.27	3.46	3.20
Flowability (s/50 g)	30.72	36.87	36.46	35.98	34.88	36.32

between the powder particles is reduced. Table 2 provides the apparent density and flowability of powders with different lubricants added. Compared with pure iron powder, the addition of alloy powder with smaller particle size in the mixture increases the friction force between powder particles in the flow process, which reduces the fluidity of powder. At the same time, fine alloy powder can be filled in the pits of iron powder surface and the pore between iron powder particles, thus improving the bulk density. Without lubricants added, the flowability and apparent density of the premixed powder are 36.87 s/50 g and 3.15 g/cm^3, respectively. The improvement of apparent density and flowability is different with various lubricants added. When EBS wax and zinc stearate were used as lubricants, the bulk density increased to 3.18 and 3.20 g/cm^3. Due to the introduction of Superlube 2.0, part of alloy powder adhered on the surface of the iron powder, and the amount of free alloy powder was reduced. Therefore, compared with EBS and zinc stearate, the powder properties were slightly improved, apparent density reaches to 3.27 g/cm^3. With the addition of new lubricant, the apparent density and flowability of mixture are much higher than those of other lubricants, reaching 3.46 g/cm^3 and 34.88 s/50 g, respectively.

Figure 7 shows the green density of compacts with different lubricants added under the pressure of 400–800 MPa. The conventional premixed powder was used as contrast. Under each compaction pressure, the green density of compacts with different lubricants added is higher than that of conventional premixed powder at varying degrees, which indicates that all lubricants can reduce the pressure loss caused by friction and improve the compacting performance of powders during compaction process. The green density of compacts with zinc stearate added is the highest at 400 MPa, reaching 6.83 g/cm^3. Under the same conditions, that of premixed powder is only 6.62 g/cm^3, 0.21 g/cm^3 lower than former. With the increase in compaction pressure, the density contrast of compacts between premixed powder and lubricant-added powder decreases gradually. Compared with the new lubricant, the density contrast between the two is only 0.08 g/cm^3 at 800 MPa. Compression pressure is the most important factor in determining compact density. Above 700 MPa, the relative density reaches 95% and the increasing effect of lubricant on green density decreases. In addition, the lubricant occupies a certain volume in the compact, which hinders the increase in green density. The mixed powder with zinc stearate added shows great compaction performance at 500 MPa, and the compact density reached 7.03 g/cm^3, equivalent to the new lubricant. Under the compaction pressure of 600–800 MPa, the lubrication effect of the new lubricant is better than that of other lubricants. The order of lubrication effect is as follows: New lubricant > Superlube 2.0 > zinc stearate > EBS. At 800 MPa, the compact density with new lubricant added reaches 7.37 g/cm^3, 0.4 g/cm^3 higher than that of Superlube 2.0. The lubrication effect can be enhanced by introducing thixotropic components in new lubricant, which leads to its excellent effect compared with EBS.

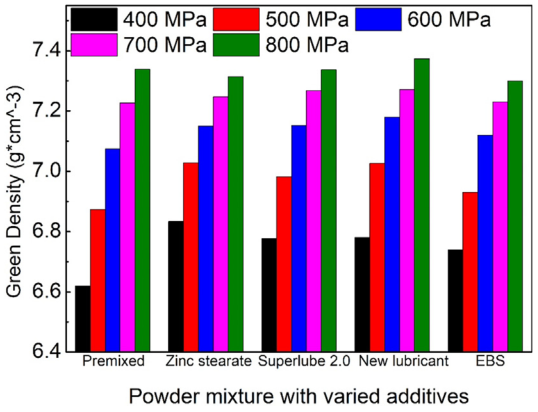

FIGURE 7

The density of compacts with different lubricants added under the compaction pressure of 400–800 MPa.

In addition to indirectly judging the lubrication effect from the green density, the ejection property is also an important parameter to measure the lubrication effect. Figure 8(a) shows the ejection pressure of compacts with different lubricants added. Consistent with the conclusion in Figure 7, each kind of lubricants can reduce the friction between die wall and compacts effectively during demolding processes, compared with premixed powder. The excellent antifriction effect of zinc stearate under various pressures is attributed to its abundance. Under 400 and 500 MPa, the corresponding ejection pressure is only 19.2 and 20.3 MPa. With the compaction pressure increased from 400 MPa to 800 MPa, the ejection pressure of compact with new lubricant added changed smoothly. The ejection pressure is 14.1 MPa at 400 MPa and 19.5 MPa at 800 MPa, only rising by 5.4 MPa. The shear thinning of polyethylene wax and polyamide wax occurs at low and high pressures respectively. During the demolding process, a film of lubricant liquid can be formed between the compact and the female mold, which is advantageous for the reduction in the ejection force. When the pressure is higher than 600 MPa, the ejection pressure of premixed powder and EBS increases explosively due to the formation of cold welding. From 600 MPa to 800 MPa, the ejection pressure increases by 17.8 MPa and 11.81 MPa. Figure 8(b) and (c) shows the ejection pressure vs. time curve with EBS and new lubricant added at 800 MPa. Compared with EBS, the fluctuation of ejection pressure disappears in the sliding process of compact with new lubricant added, further reflected its excellent lubrication performance.

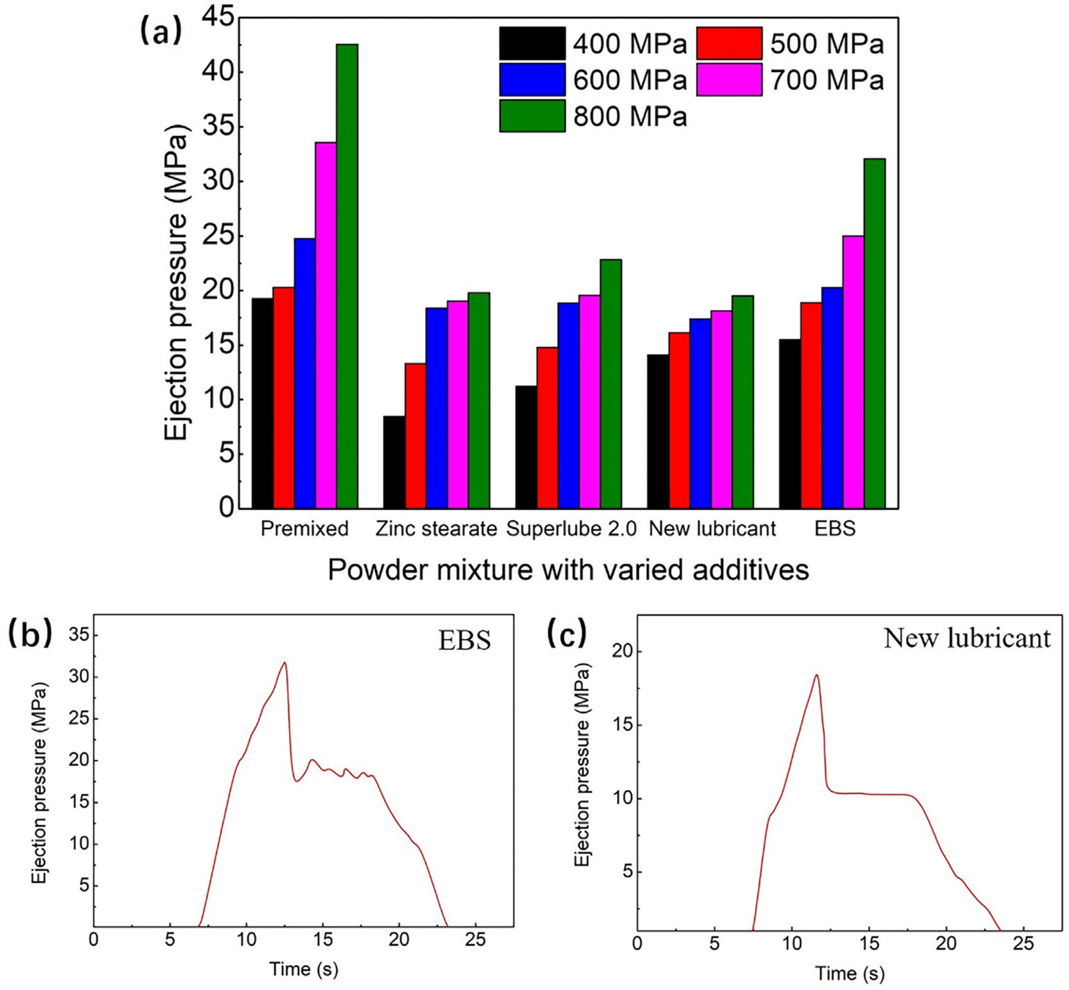

FIGURE 8

The ejection pressure of compacts with different lubricants added (a) and ejection pressure vs. time curve with EBS (b) and new lubricant (c) added at 800 MPa.

4. Conclusions

(1) The thixotropy components in the lubricant are polyethylene wax and polyamide wax, EBS and stearic acid have almost no thixotropic behavior, causing the absence of thixotropic-loops. The thixotropic properties of polyethylene wax and polyamide wax is reflected at low and high pressures, respectively. When the compaction pressure increases from 400 MPa to 800 MPa, the polyamide wax content corresponding to the maximum green density increases from 0% to 30%.

(2) With the addition of new lubricant, alloying additives are effectively filled into the pits of iron particles, which enhance the smoothness of iron powder. And the apparent density and flowability of mixture are much higher than those of other binders, reaching 3.46 g/cm^3 and 34.88 s/50 g, respectively.

(3) Under the compaction pressure of 600–800 MPa, the lubrication effect of the new lubricant is better than that of EBS, zinc stearate and Superlube 2.0. When the content of both polyamide wax and polyethylene wax was 20%, the green density of compacts reaching 7.18 g/cm^3 at 600 MPa and 7.37 g/cm^3 at 800 MPa.

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