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Effects of stearic acid on synthesis of nanocomposite WC–MgO powders by mechanical alloying

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Abstract The effects of stearic acid as a process control agent (PCA) on the synthesis of WC–MgO by mechanical alloying have been investigated. 0–2.0 wt% of stearic acid is added into the mixture of WO_3, Mg, and graphite powders in high-energy planetary ball milling experiments, and the as-milled powders are characterized by XRD and TEM. Results show that the mechanochemical reaction among WO_3, Mg, and graphite to form WC–MgO can be changed from a mechanically induced self-propagating reaction (MSR) to a gradual reaction by the addition of stearic acid in the range from 1.2 to 1.8 wt%, when other milling parameters are maintained at the same level. It has also been found that with the addition of stearic acid, the crystallite and particle size of WC–MgO powders can be refined, the homogeneity of particle size can be improved and the powder yield can be increased.

Introduction

Mechanical alloying (MA) has been considered as an effective and practical way to fabricate various advanced nanocomposite powders owing to its advantages in low cost, simple technology, and equipment [1–3]. El-Eskandarany [4, 5] first adopted this technique to ball mill the WO_3, Mg, and graphite mixture powders. Nanocomposite WC–MgO powders were obtained at room temperature through the mechanochemical reaction among the reactant powders induced by high-energy ball milling, which were successively consolidated into bulk material using plasma-activated sintering. Results show that this consolidated nanocomposite WC–MgO material offers a unique combinations of super hardness and excellent fracture toughness. However, further studies [6, 7] carried out at Donghua University indicated that the mechanochemical synthesis of nanocomposite WC–MgO from WO_3, Mg, and graphite always completes through a mechanically induced self-propagating reaction (MSR). In addition, a significant portion of coarse WC–MgO crystallites and particles may form under the high temperature caused by MSR. Furthermore, the powder yield is low as many powders get adhere to the milling balls and vial, which is difficult to be detached.

There are two possible methods to prevent the combustion reaction and the severe welding, one is to lower the temperature of the milling vial [8–10], and the other is to add stearic acid as a process control agent (PCA) to the reactant powders [11, 12]. The effects of stearic acid on the ball milling process of CuO–Ca/Ni, Ti–BN, and Al–Mg systems have been investigated by Schaffer et al., Byun et al., and Lu and Zhang, respectively [13–15]. Results show that with the addition of stearic acid, the occurrence of combustion reaction can be successfully delayed or suppressed, the interparticle welding during collisions can be inhibited, and the particle size can be decreased. It may be noted that a combustion reaction should be avoided if one is interested in producing the materials in nanocrystalline state. Another requirement for formation of nanocrystalline powders is that the volume fraction of the by-product phase must be sufficient to prevent particle agglomeration [16].

In the present paper, in order to understand the effects of stearic acid on the WO_3–Mg–C ball milling system, the

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effects of stearic acid and its amount on the mechanochemical formation mechanism, the microstructure and powder yield of WC–MgO powders have been systemically investigated, and the suppressing of stearic acid on MSR has also been discussed.

Experimental procedure

Reactant mixture powders used in this study were commercial powders of WO_3 (1 μm, 99.9%), Mg (50 μm, 99.5%), and graphite (3 μm, 99.9%). These powders were mixed at an atomic ratio of 1:3:1. The WO_3–Mg–C mixture was charged together with stearic acid and cemented carbide alloy balls (10 mm in diameter) into a hard alloy vial (250 mL in volume). The amount of stearic acid was controlled from 0 to 2.0 wt%. The ball milling experiments were carried out using a QM-1SP4 planetary ball milling machine under argon gas atmosphere at milling speed of 350 rpm and ball-to-powder weight ratio of 10:1. The milling experiments were interrupted and small amount of powders were taken out in air at several intervals for analysis. The phase of the milled composite powders had been analyzed by XRD with CuK_α radiation, and the crystallite size and the homogeneity of particle size were investigated by TEM operating at 200 kV.

Results

Effect of stearic acid on the mechanochemical reaction

Figure 1 shows the XRD patterns of WO_3–C–3Mg mixtures milled without stearic acid for various milling time. It can be seen from Fig. 1a, b that in the previous 5 h of ball milling, only the WO_3, Mg, and C peaks could be detected. When milling for 5.5 h, the WO_3–Mg–C mixture abruptly reacted to form WC–MgO powders, the peaks corresponding to the reactant powders disappeared, which indicate the completeness of the reaction (Fig. 1c). Figure 1d, e demonstrates that WC and MgO are still the main products, and no new peaks can be observed in the XRD patterns with the milling time extending to 80 h. The reaction during ball milling could be represented as

$$WO_3 + C + 3Mg \rightarrow WC + 3MgO \quad (1)$$

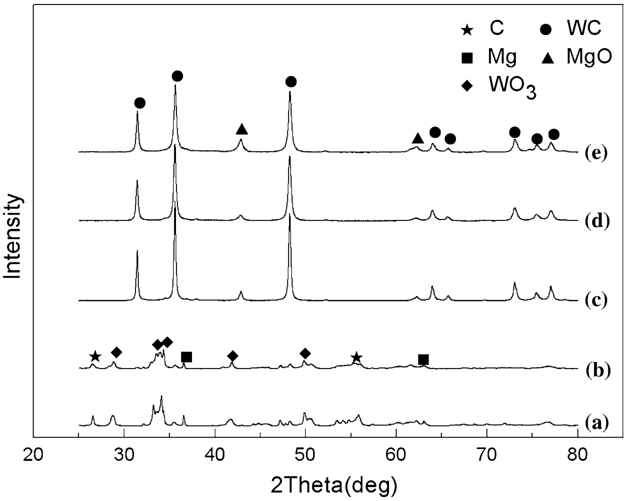


Fig. 1 XRD patterns of powders milled without stearic acid for (*a*) 0, (*b*) 5, (*c*) 5.5, (*d*) 30, and (*e*) 80 h

Slight explosion sound could be heard after milling for 5.5 h under above milling conditions, and the temperature of the milling vial reached a very high level almost at the same time, as shown in Fig. 2a. These phenomena indicate that the occurred reaction (1) is a mechanically induced self-propagating reaction. Figure 2b shows the TEM micrograph for the agglomerated powder which resulted just after the temperature peak. The particles in Fig. 2b are coarse and most of the size is above 100 nm.

The above MSR always results in the formation of coarse WC–MgO particles and low powder yield. With the aim of preventing MSR, stearic acid is added as a PCA. Figure 3a shows the XRD patterns of WO_3–C–3Mg system milled with 1.1 wt% of stearic acid for different milling times. It indicates that reaction (1) abruptly occurred to form WC–MgO after about 12.3 h of milling, which illuminates that MSR can be delayed rather than entirely suppressed by adding 1.1 wt% of stearic acid. The XRD patterns of the powders milled with 1.4 wt% of stearic acid is shown in Fig. 3b. In the initial stage of ball milling process, there are also only existing WO_3, Mg, and C peaks, whose intensities decrease gradually with milling time. New peaks corresponding to WC and MgO can be observed after a milling time of 40 and 50 h, coexisting with WO_3, Mg, and C peaks. No peak of reactant materials can be detected up to 80 h of milling, suggesting the completion of the reaction. This steady process can be expressed by the gradual reaction mode as the reactants and product coexist for a long period, which is about 80 h in the present milling conditions. In addition, Fig. 3c shows that WC–MgO cannot be successfully synthesized up to 100 h of ball milling with the addition of 2.0 wt% of stearic acid, when the other milling parameters are maintained at the same level. Figure 3d demonstrates that when 1.1 wt% of stearic acid is added, the temperature of vial surface abruptly rise from 27.5 °C to about 39 °C after 12.3 h of ball milling, and drop to 27.5 °C soon. This rapid temperature rise may be caused by the mass combustion heat liberated from MSR. Whereas, when 1.4 wt% of stearic acid is added, the temperature of vial surface is maintained at 27 °C approximately, and no such sharp

Fig. 2 **a** Temperature variation of milling vail during milling for reaction (1) and **b** the corresponding TEM micrograph

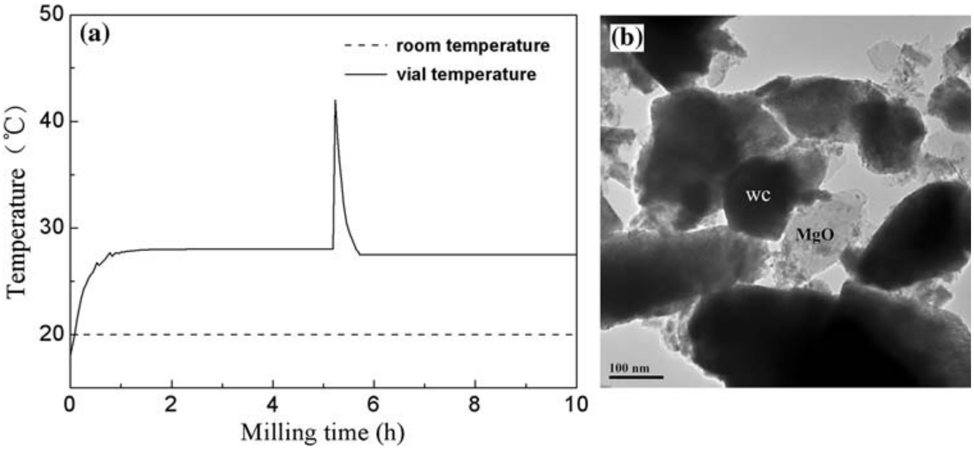
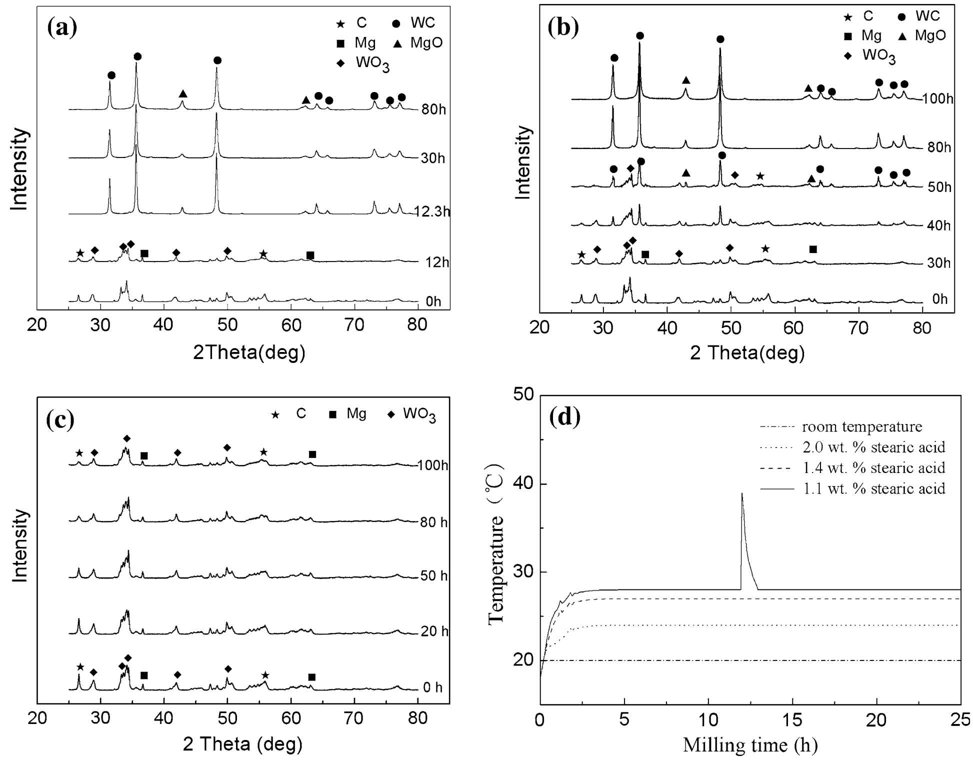


Fig. 3 XRD patterns of powders milled with **a** 1.1, **b** 1.4, **c** 2.0 wt% stearic acid, and **d** the temperature variation of vial surface with milling time



temperature peak can be observed, which indicates that the reaction proceeds in a gradual way. However, 27 °C is still a little bit higher than the value measured at the condition that up to 2.0 wt% of stearic acid is added.

Figure 4 indicates that the incubation time for the MSR, i.e., the time from the beginning of milling to the occurrence of MSR, depending on the concentration of stearic acid. The incubation time is about 5.5 h without stearic acid and there are some changes up to 0.8 wt% of stearic acid. The addition of stearic acid of between 1.1 and 1.2 wt% further increases the incubation time, but the MSR still occurs. When 1.2 wt% of stearic acid is added, however, the MSR is suppressed in two experiments while it occurs in another two. With over 1.2 wt% of stearic acid, reaction (1) always proceeded gradually. Therefore, the critical concentration of stearic acid to inhibit the MSR of reaction (1) is about 1.2 wt%.

Figure 5 shows the XRD patterns of the powders with different amounts of stearic acid after 80 h milling. When the concentration of stearic acid is lower than 1.2 wt%, there is no distinct difference in the XRD patterns of the powders, as shown in Fig. 5a–c. However, it can be found from Fig. 5d, e that with over 1.2 wt% of stearic acid, both WC and MgO peaks broaden much more, which means that the suppression of MSR contributed to the reduction of the crystallite size. The average crystallite sizes of WC and

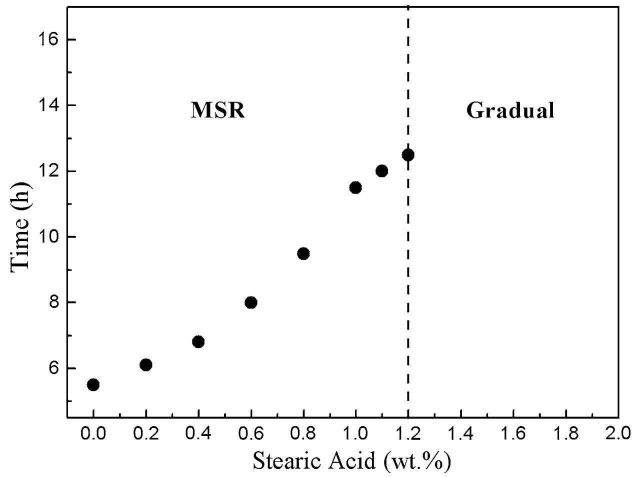


Fig. 4 Incubation time for MSR with different amount of stearic acid

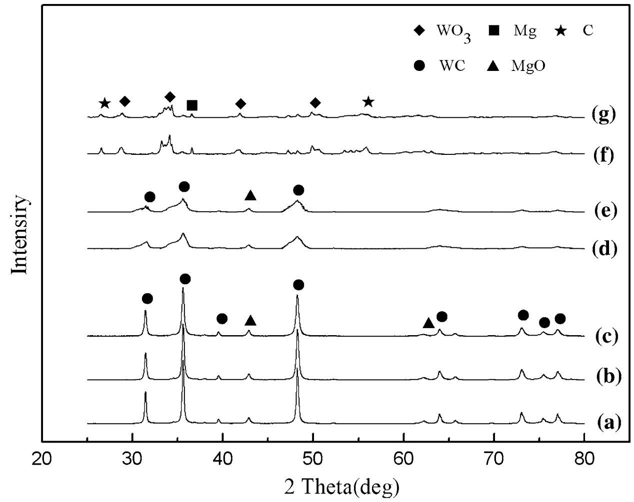


Fig. 5 XRD patterns of powders milled for 80 h with (*a*) 0, (*b*) 0.8, (*c*) 1.1, (*d*) 1.4, (*e*) 1.8, (*f*) 2.0, and (*g*) 2.2 wt% of stearic acid

MgO, estimated by Scherrer's formula, are 19 and 29 nm without stearic acid, and 10 and 15 nm with 1.4 wt% of stearic acid, respectively, under the same milling conditions. Nevertheless, with over 2.0 wt% of stearic acid, WC–MgO cannot be successfully formed up to 100 h of ball milling, as shown in Fig. 5f, g.

It can be found from the above results that the critical concentration of stearic acid to change reaction (1) from MSR to a gradual reaction is about 0.27 mol% (1.2 wt%). In general, the change of reaction mode by an inert addictive is attributed primarily to two mechanisms, i.e., increasing the heat capacity (C_p) and decreasing the contact area between the reactants [17, 18]. Munir [19] proposed a simple guideline to decide whether or not a self-propagating reaction might occur for a certain system. According to his proposal, the reaction can start without additional energy from an exterior source when the adiabatic temperature rise ($-\Delta H/C_p$) is above 2000 K. The C_p can be increased when 1.2 wt% of stearic acid is added, then the $-\Delta H/C_p$ of reaction (1) calculated from the thermodynamic date will be decreased from ~6000 K to ~5800 K, under which the MSR would still occur. Thus, it seems that the suppression of the MSR by stearic acid is primarily owing to the decrease in contact area among the reactants. The stearic acid, being absorbed on the surface of reactant powders, helps decreasing the contact area among them, which leads to the slowing down of the reaction rate and therefore either delays or completely suppresses the MSR. However, the contact area may be too little to initiate reaction (1), if excessive (>1.8 wt%) stearic acid absorbed on the surface of reactant powders. It should be noted that such an amount is too small to consider the possibility that change the reaction mode could be induced by other reactions, as there is no other phase can be observed in the XRD patterns, as shown in Fig. 5.

Gradual reaction results in a fine crystallite size of WC and MgO, which can be easily understood by the reason that there is no large temperature rise as the most reaction heat liberated during the steady reaction process. Furthermore, for the MSR, after a certain time of milling, the combustion reactions abruptly occur to produce WC and MgO, and finally further milling reduces the crystallite. While in the gradual reaction process, the WC and MgO products forming in a gradual reaction and coexisting with unreacted WO_3, C, and Mg for a long time, which is advantageous for forming finer particles compared with simply milling two phases of WC and MgO together.

Effect of stearic acid on the microstructure of powders

With the aim to investigate the effect of stearic acid on the microstructure of the mechanical alloyed powders, the powders milled with 0, 1.1, and 1.4 wt% of stearic acid for 80 h are characterized by TEM, as shown in Fig. 6. These three powder samples all contain two phases: the first phase WC appears as deep-black grains, while the second phase MgO consists of light-gray grains. The images in Fig. 6a indicates that the crystallite size of WC and MgO milled without stearic acid is rather large and inhomogeneous, in great part are above 50 nm, even approaches to 100 nm. The crystallite size of powders milled with 1.1 wt% of stearic acid can be a little decreased and its homogeneity of particle size can be slightly improved either, as shown in Fig. 6b. The reaction mode can be changed from MSR to gradual reaction when the concentration of stearic acid is increased to be 1.4 wt%. Figure 6c shows that there are no such large crystallites and the sizes of the homogeneously distributed WC and MgO crystallites are much smaller, mostly are between 10 and 25 nm. Thus, the average crystallite size and agglomeration can be considerably

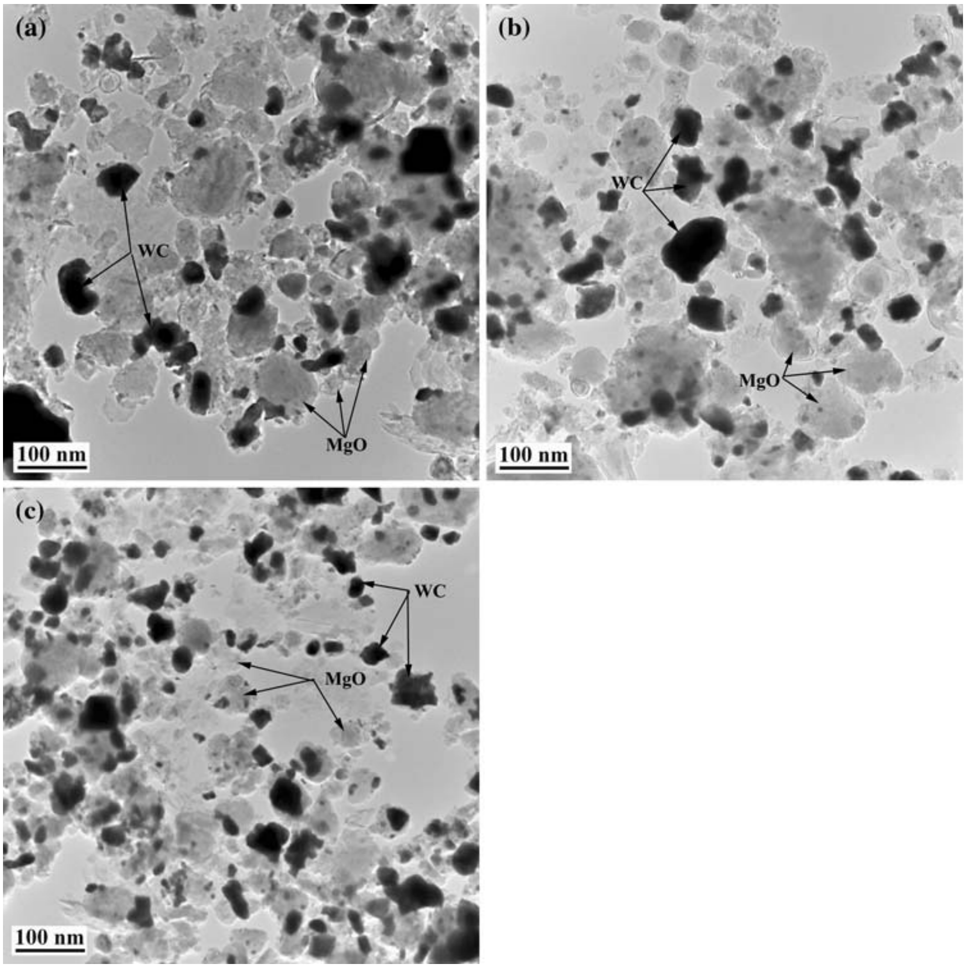


Fig. 6 TEM pictures of powders milled for 80 h with **a** 0 wt%, **b** 1.1 wt%, **c** 1.4 wt% of stearic acid

decreased and the homogeneity of particle size can be obviously improved when the amount of stearic acid is enough to suppress the occurrence of MSR.

In the milling process, considerable plastic deformation of MgO powders greatly enhance the surface activity, thus the neighboring powder particles may get together to reduce the surface activity, which can hinder the refinement and MA of the processing powders. When an appropriate amount of stearic acid is added into the reactant powders during ball milling, stearic acid will adsorb onto the fresh surface to decrease the surface activity and inhibit the conglomeration of powders, because adsorption is a free energy self-decreasing process. Figure 6 suggests that the microstructure of powders can be improved with the addition of stearic acid, however, there is no obvious effect unless the amount of stearic acid is enough to change the reaction mode from a MSR to a gradual reaction. This can be expressed by the reason that the vial surface temperature may be maintained at a low level during the synthesis process of WC–MgO through steady gradual reaction, which is in favor of obtaining homogeneously distributed fine particles and crystallites. While the vial surface temperatures may reach a very high value due to the excessive combustion heat liberated during MSR process, and these temperatures lead to the conglomeration and formation of large particles of the reaction products.

Effect of stearic acid on the powder yield of powders

Powder yield is one of the most important indicators to estimate milled powders recovered after ball milling, which is commonly expressed by the ratio between the weight of powders after and before ball milling. Powder yield also can quantificationally reflect the adhering degree of powders during MA. Figure 7 shows the relation between powder yield and the amounts of stearic acid added.

It can be found from Fig. 7 that the powder yield can be greatly enhanced to be 80.6% when 1.8 wt% of stearic acid is added, as other milling parameters are maintained at the same value. After 80 h of ball milling, fine WC–MgO powders can be obtained, and both the surfaces of vial and milling balls are bright and clean, nearly no adhering phenomenon can be observed. On the other hand, the

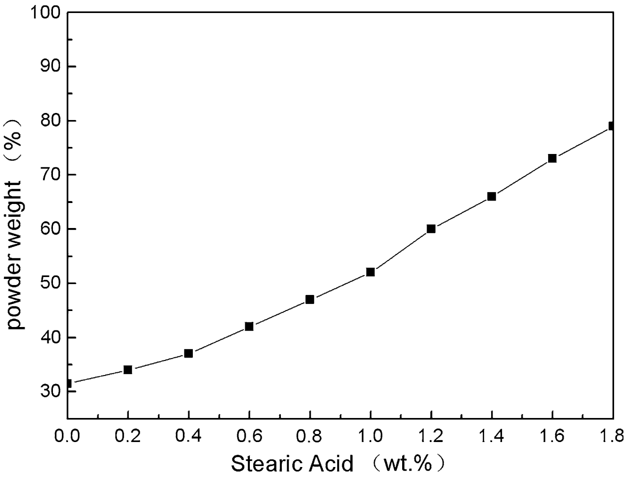


Fig. 7 Relation between powder product yield and the amounts of stearic acid added

powder yield is only 31.5% when milled without stearic acid under the same milling conditions. The end powders exhibit with large grain size, and a great quantity of powders get coated onto the surface of the milling balls and vial. While no WC–MgO powders can be formed when over 1.8 wt% of stearic acid is added, therefore the powder yield under this milling condition have not been discussed in the present work.

During ball milling process, constant collisions among milling balls, powders, and milling vial result in the plastic deformation of the MgO powders. Small parts of MgO powders get cold welded onto the milling balls and vial, while a great part of MgO powders particles are refined by work-hardening. Due to the increase of the surface activity, the refined powders will be inclined to get together and coated onto the milling balls and vial spontaneously. This is a process in which the free energy gets decreased. Therefore, the adhering of ductile powders to the milling balls and vial is unavoidable when milled without stearic acid. A very thin "protective film" between the powders and the milling balls/vial may form with the addition of stearic acid. This "protective film" prevents the contact between the powders and the milling balls/vial, which decreases the abrasion of milling balls, as well as reduces the adhering of powders to the milling balls and vial. Moreover, the adsorption of stearic acid on the powder surface can also decrease the surface energy of powder particles, and diminishes the adsorption driving force of powders to the milling balls and vial, consequently reduces the possibility of adhering of powders to the milling balls and vial. As a result, the addition of stearic acid can greatly increase the powder yield, which is an important method to overcome the adhering problem during the process for synthesizing nanocomposite WC–MgO powders.

Conclusion

(1) The crystallite and particle sizes of WC–MgO powders can be refined, the homogeneity of particle size can be improved and the powder yield can be enhanced with the addition of stearic acid as a PCA.
(2) The mechanochemical reaction among WO_3, Mg and C reactant powders to form nanocompostite WC–MgO powders can be changed from a MSR mode to a gradual reaction by adding over 1.2 wt% of stearic acid.
(3) The WC–MgO powders synthesized through gradual reaction are possessed of finer crystallites and more homogenous particle size distribution. Furthermore, compared with the unstable MSR, the steady and controllable gradual reaction is more suitable to be applied to the practical production.

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