Effect of high-energy attrition milling and La$_2$O$_3$ content on the microstructure of Mo-La$_2$O$_3$ composite powders

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Abstract. Mo-La$_2$O$_3$ composites are potential high-temperature materials for future technology devices operating at temperatures above 1300 °C because of their excellent thermal stability, high mechanical properties and good creep resistance. In this study, we focused on the preparation of Mo-matrix/lanthanum oxide (La$_2$O$_3$) composite powders using high-energy attrition milling. The effects of rotational milling speed (350 and 800 rpm) and La$_2$O$_3$ content (2.5 and 10 vol. %) on the microstructural evolution, phase composition, morphology, and distribution of the second phase in the produced composite Mo-La$_2$O$_3$ powders were investigated in details. The results show that the most interesting composite powder was Mo-10 vol.% La$_2$O$_3$ produced using a rotational speed of 800 rpm, which exhibited better distribution, smaller particle size and higher amount of ceramic phase introduced in the interiors of the Mo grains.

1 Introduction
At present, in connection with the upcoming power and energy engineering technology improvements, a lot of attention is drawn to the development of materials with superior chemical, physical and mechanical properties at elevated temperatures. Molybdenum (Mo) alloys and Mo-based composites are promising high-temperature materials to be applied in aerospace, energy generation processes, electronics, telecommunication, and defense fields. The reason for that is the combination of very high melting point (~2623 °C), good creep strength at elevated temperatures, high thermal conductivity (138 W·m$^{-1}$·C$^{-1}$), low specific heat (25.1 - 28.4 J·K$^{-1}$·mol$^{-1}$), comparable density to the Ni-superalloys, etc. [1]. The application of Mo-based alloys and composites in aerospace engines and ground-based stationary gas turbines can be a cost-effective solution to increase their efficiency and to decrease their environmental impact due to reduced amount of CO$_2$ emitted into the atmosphere. However, low
oxidation resistance and ductile-to-brittle transition behavior of Mo and its alloys are to be improved to ensure the best performance in the aforementioned applications [2].

Several approaches were employed, including substitutional alloying by silicon and boron as well as the second phase strengthening with oxide (ZrO₂, La₂O₃, etc.), carbide (TaC, ZrC), or other (Mo₅Si, Mo₅SiB₂) reinforcements [3-6]. The introduction of rare-earth elements’ oxide (REOs) particles, such as La₂O₃, into Mo-based composite microstructure leads to their significant strengthening, creep resistance enhancement, and oxidation resistance improvement due to strong metal-REOs-oxygen connection. The REOs particles might play role of the barrier for the grain size growth, increasing the ductility, toughness, strength, and elastic modulus, which in turn reduces the ductile-to-brittle transition temperature (DBTT). The studies on the preparation of the Mo-based composites by high-energy milling are rather scarce [7-8] and still need to be performed systematically. In this context, the attrition milling is an attractive method for production of Mo-La₂O₃ composite powders, which then can be potentially used for thermal spray or advanced sintering (e.g., spark plasma sintering). Due to intensive impact and shearing action occurring in this type of milling, effective and homogenous particle refinement results in obtaining pure and ultra-fine powder particles (as small as 20 nm) of solid materials with uniform microstructure and improved properties [9-10].

The present work studies the preparation of the composite Mo-matrix powder with 2.5 and 10 vol. % of lanthanum oxide (La₂O₃), using two different rotation speed in rotational high-energy ball mill. Particle morphology, microstructure and phase composition of the fabricated composite powders were examined and analyzed in detail.

2 Materials and methods
For the fabrication of the Mo-based experimental powder composition with 2.5 and 10 % vol. of La₂O₃, the commercially available 45-90 μm molybdenum (GTV, Germany) and 99.3 % pure lanthanum oxide (Luoyang Golden Egret Cetools Co., China) powders were utilized. Composite powder mixtures were prepared by measuring of tap density of ceramic powders, considering the volume of 140 g of molybdenum powder. The powder mixtures were processed in the high-energy attrition ball mill Simoloyer CM01 (Zoz Gmbh, Germany) in ambient atmosphere. The ball-to-powder ratio was kept at 100:6, using stainless steel balls with 4.5 mm in diameter. Prior to the powder processing, pre-milling and homogenization of powder mixtures was provided by mixing at 700 rpm for 5 minutes, adding ~0.5 ml of isopropyl alcohol as a lubricant. For the final processing, the low- and the high-speed rotation modes conducted at 350 rpm and 800 rpm, respectively, for 60 minutes were used (Table 1).

| Designation of the powder | Chemical composition | Milling parameters | Final milling |
|--------------------------|----------------------|-------------------|--------------|
| Mo-La₂.5-350             | Mo – 2.5 vol.% La₂O₃ | Mo – 1.05 wt.% La₂O₃ | 700 rpm, 5 min | 350 rpm, 60 min |
| Mo-La₁₀-350              | Mo – 10 vol.% La₂O₃ | Mo – 4.2 wt.% La₂O₃ | 700 rpm, 5 min | 350 rpm, 60 min |
| Mo-La₂.5-800             | Mo – 2.5 vol.% La₂O₃ | Mo – 1.05 wt.% La₂O₃ | 700 rpm, 5 min | 800 rpm, 60 min |
| Mo-La₁₀-800              | Mo – 10 vol.% La₂O₃ | Mo – 4.2 wt.% La₂O₃ | 700 rpm, 5 min | 800 rpm, 60 min |

The morphology of powder particles in the fabricated composite powders and their elemental analysis were studied by means of scanning electron microscope LYRA 3 (SEM; Tescan, Czech Republic) equipped with X-ray energy dispersive spectroscopy (EDX) detector XFlash 5010 (Bruker, USA). EDX analysis was performed onto 5 areas at least. To exclude electrostatic charging, prior to SEM and EDX study, powder particles were covered by thin carbon layer (~25 nm) using EM ACE 600 coater (Leica Microsystems, Germany). Phase composition of initial and fabricated powders was determined by X-ray diffraction analysis using SmartLab 3kW diffractometer (Rigaku, Japan) by
scanning in Bragg-Brentano geometry using Cu Kα radiation (50 kV, 50 mA) for the scanning 20 range between 10-90° at 3 °/min.

3 Results and discussion

2.1 Initial powders
XRD analysis of the commercially purchased molybdenum and lanthanum oxide powders showed that they were single-phase materials (Figure 1a). Molybdenum and lanthanum oxide powders showed body-centred cubic (ICSD 65-007-6279) and hexagonal (ICSD 98-015-4586) crystallographic lattices, respectively.

Scanning electron microscopy revealed that Mo powder particles morphology is related to the agglomerated and sintered type with spherical-shaped agglomerates of 30-80 µm composed from fine particles (Figure 1 b). Analysis of the initial La2O3 powder showed irregularly shaped particles in the range of 4-20 µm (Figure 1 c).

![Figure 1. Phase composition (a) and morphology of (b) Mo and (c) La2O3 initial powders.](image)

2.2 Effect of milling
The XRD investigation of fabricated composite powders did not detect any intermediate LaXMoYOZ compounds after milling in both milling modes, as shown in the example of the composite with 10 vol. % of La2O3 (Figure 2). It means that no chemical reaction or alloying occurs between Mo and La2O3 during low- and high-energy milling conditions. At the same time, the appearance of lanthanum hydroxide La(OH)3 shows that the hydroxylation of La2O3 compound occurs during milling, which is probably due to milling in ambient conditions or use the isopropyl alcohol lubricant. The occurrence of the hydroxide is typical in the chemistry of the lanthanum oxide, moreover, the hydroxide easily decomposes to the oxide by heat treatment around 300°C [11]. Furthermore, after the milling in the high-energy milling mode, a slight half-width peak broadening has been observed along with slight decrease of the peak intensity for all the samples. It can be explained by higher deformation of Mo matrix during milling as well as refinement of La2O3 particles. As both Mo and La2O3 are easy mechanically deformable [12], intensive deformation during high-energy milling might provide interaction between ceramic and metallic phases with further improvement of grain refinement of molybdenum matrix.
Figure 2. Phase composition of Mo-La10-350 (red line) and Mo-La10-800 (black line) powder mixtures after milling.

The effect of the milling processing using 350 rpm and 800 rpm onto the composite powder morphology is shown in Figure 3. The low-energy milling of Mo-La2.5-350 and Mo-La10-350 powder samples resulted mostly in the refinement of Mo and La$_2$O$_3$ particles, while the formation of larger flake-like powder agglomerates from the deformed and welded Mo particles and crushed La$_2$O$_3$ did not occur readily. In contrast, during high-energy milling, higher delivered energy to the powder system (samples Mo-La2.5-800 and Mo-La10-800) resulted in the formation of large amount of cold-welded particles agglomerates of ~20-50 µm in size, whose number was the highest in the Mo-La10-800 sample.

Figure 3. Morphology and details of fabricated (a-b) Mo-La$_2$O$_3$-350 and (c-d) Mo-La$_2$O$_3$-800 powders.
These agglomerates, which were formed due to intensive plastic deformation, exhibited the formation of flake-like particles with lamellar microstructure (Figure 4). The detailed SEM morphology shows the presence of molybdenum lamellas (light-gray color) with irregular-shaped submicron-sized lanthanum oxide particles located on the grain boundaries (dark-gray color). When comparing the results of the low- and the high-energy milling, it can be seen that the number of flake-shaped particles is higher and the lamellas in the microstructure are thinner or refined with incorporated $\text{La}_2\text{O}_3$ particles in between. EDX mapping also confirms more intensive incorporation of ceramic particles as well into the agglomerates in high-energy milling mode, while in the low-energy milling mode the most of $\text{La}_2\text{O}_3$ crushed debris is located in between deformed Mo particles. Furthermore, in the agreement with intensive incorporation of $\text{La}_2\text{O}_3$ particles into Mo matrix during high-energy milling, EDX elemental analysis showed almost twice higher content of La element in the Mo-La$_{2.5}$-800 and Mo-La$_{10}$-800 powders, Table 2.

To summarize, the observed powder microstructure after the mechanical milling processing will definitely impact the mechanical properties of the final sintered product. In this way, powder particles with refined molybdenum matrix produced by high-energy attrition milling are likely to have uniformly distributed lanthanum oxide particles. Besides the reinforcement of the molybdenum, uniformly distributed ceramic particles can reduce the ductile-to-brittle-transition as well that is one of the main aims of the Mo-focused research. However, even though it was possible to produce composite powder particles, further research on formation of spherical shaped composite powder particles is needed, following to the potential application in thermal spraying where the shape of the feedstock powder particles plays significant role.

![Figure 4. EDX elemental mapping of (a) Mo-La10-350 and (b) Mo-La10-800 composite powder particle cross-cuts.](image)

**Table 2.** EDX elemental composition of the Mo-La$_2$O$_3$ composite powder agglomerates.

| Designation of the powder | Element (wt. %) |
|--------------------------|-----------------|
|                          | Mo  | O   | La   |
| Mo-La2.5-350             | 81.1| 18.4| 0.5  |
| Mo-La10-350              | 81.6| 15.8| 2.6  |
| Mo-La2.5-800             | 80.1| 19.1| 0.8  |
| Mo-La10-800              | 84.1| 11.0| 4.9  |
Conclusions

- In the present work, high-energy attrition ball milling has been employed for the preparation of Mo-La$_2$O$_3$ composite powders with low (2.5 vol.%) and high (10 vol.%) content of La$_2$O$_3$ phase. The most interesting powder composition for further powder consolidation experiments was obtained from Mo-10 vol.% La$_2$O$_3$ mixture using the high-energy ball milling mode at 800 rpm for 60 min, while the use of lower La$_2$O$_3$ content and low-energy milling resulted mostly only in deformation of Mo and crushing of La$_2$O$_3$ particles.
- Composite Mo-La$_2$O$_3$ powder agglomerates show flake-like particles with lamellar microstructure with the uniformly distributed submicron-sized ceramic particles on the grain boundaries, which should beneficially affect the mechanical properties and DBT temperature of the final products sintered from this powder.
- As one of the potential applications of this powder is thermal spraying feedstock, further research on formation of composite powder particles in spherical shape is definitely needed.

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