Direct Laser Deposition of 14Cr Oxide Dispersion Strengthened Steel Powders Using Y$_2$O$_3$ and HfO$_2$ Dispersoids

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Abstract: This study investigated the feasibility of using HfO$_2$ as a dispersoid in the additive manufacturing process, compared to Y$_2$O$_3$. The effect of pre-annealing treatment was investigated too. Scanning electron microscopy (SEM) analyses revealed unusually coarse deposition layers for both the HfO$_2$ and Y$_2$O$_3$ dispersed oxide dispersion strengthened (ODS) steels, in both the as-milled and the pre-annealed conditions. The deposited layer of the HfO$_2$ dispersed ODS steel had relatively coarser grains than the deposited layer of the Y$_2$O$_3$ dispersed ODS steel in both the as-milled and the pre-annealed conditions. Moreover, the SEM results also revealed the presence of nanometer sized particles in all the deposition layers of both Y$_2$O$_3$ and HfO$_2$ dispersed ODS steels, and their number densities were far lower than those in conventional bulk ODS steels. However, transmission electron microscopy analyses revealed that the dispersion and retention of nanoparticles within the melt were not achieved, even with HfO$_2$ as a dispersoid, in contrast to the results from the SEM analyses. Furthermore, the deposition layers of both the as-milled Y$_2$O$_3$ and HfO$_2$ ODS steels also exhibited an unusual nano-grained structure. The microhardnesses of the HfO$_2$ and the Y$_2$O$_3$ dispersed ODS steels in both the as-milled and the pre-annealed conditions were higher than the substrate. Furthermore, the Y$_2$O$_3$ dispersed ODS steel had a higher microhardness than the HfO$_2$ dispersed ODS steel in both the as-milled and the pre-annealed conditions.

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1. INTRODUCTION

Oxide dispersion strengthened (ODS) steels have been widely developed in recent years for high temperature applications [1,2]. ODS steel is preferred as a material for fuel cladding tubes in fast breeder reactors, an application that requires a low swelling rate and high creep strength in the temperature range of 400-800 °C [3–6]. These ODS materials are usually produced by mechanical alloying followed by hot isostatic pressing (HIP) or hot extrusion [1,7,8]. However, the powder metallurgy based production method results in high cost and is characterized by difficulties during manufacturing.

Technological advancements in additive manufacturing (AM) techniques have recently presented a potentially efficient and practical means of fabricating ODS steels [9]. In the AM process, object formation is achieved by adding layer-upon-layer of various materials [10,11]. Until now, research studies on the AM process of fabricating ODS steels are very limited. Clear understanding of the relationships between the AM processing parameters, heat-treatment, dispersoid, and powder quality are not yet available.

The direct laser deposition (DLD) technique, also known as direct energy deposition or direct metal deposition, has attracted attention among the various AM processes because the DLD process has many advantages over the selective laser melting (SLM) process for the production of ODS steels [12]. Among some of its advantages, it permits the use of irregularly shaped powders, has a higher deposition rate and a relatively wider processing window.

A previous work by Walker et al. [13], studied the use of the SLM process on PM2000. They demonstrated that a relatively fine distribution of Y$_2$O$_3$ oxide particles with a
mean particle size of 50–60 nm was retained in the built walls. Boegelein et al. researched further to examine the microstructure and tensile properties of the built walls [14,15]. They used Y₂O₃ as the dispersoid because Y₂O₃ is known to be very effective in the formation of stable oxide particles such as Y₂Ti₂O₇ or Y₂TiO₅.

In the production of ODS steels, retention of nanoparticles (NPs) is of prime importance. However, melting of the ODS material is generally known to be detrimental to the steel’s high temperature mechanical properties because strong capillary and inter-particle forces in the liquid state aggressively promote NPs agglomeration [16]. Furthermore, the oxide NPs tend to be removed from the microstructure due to the buoyancy effect and then slag off the surface of the melt pool [13]. To address these issues, increasing the wettability of the NPs with liquid Fe–Cr alloys [17] or using a heavier oxide as the dispersoid, can be advantageous.

HfO₂ is a heavy material compared to Y₂O₃ and its diffusivity is accordingly lower. In addition, the melting point of HfO₂ is 333 °C higher than that of Y₂O₃, which can greatly increase the stability of NPs in the melt. However, fundamental research on the effect of using a heavier oxide has not been conducted so far.

In this study, the feasibility of using HfO₂ as a dispersoid in the AM process with the DLD technique was studied, and compared to the use of Y₂O₃. In addition, the effect of pre-annealing treatment, which is normally performed to stabilize the complex oxide particles during the conventional powder metallurgy process, was also investigated.

After the DLD process, the stability and the morphology of the NPs of the Fe-Cr based ODS steel were quantitatively examined.

2. MATERIALS AND EXPERIMENTAL DETAILS

Figure 1 presents a scanning electron microscope (SEM) image of the as-received stainless steel powder, which had a nominal composition of Fe-14Cr-2W-0.35Ti (wt%). The stainless steel powder was blended with 0.3 wt% Y₂O₃ or HfO₂ powders, respectively. The mean particle sizes of the Y₂O₃ and the HfO₂ powders were 40 and 60 nm, respectively. 25 g of each blended powder was placed into a steel jar under high purity Ar atmosphere. Mechanical alloying (MA) was then carried out with a high-speed planetary ball milling machine. Rotating speed was 820 rpm and the total duration of the MA was 90 minutes. The weight ratio of the 8 mm diameter stainless steel balls to the powder mixture was 20:1.

After the MA, approximately half of the as-milled powders were annealed at 1100 °C for 1 hour under a vacuum condition of 10⁻⁶ torr. These pre-annealed samples were designated ‘pre-annealed Y₂O₃’ and ‘pre-annealed HfO₂’. The remaining halves of the two sets of powders which had not received any prior heat-treatment were designated ‘as-milled Y₂O₃’ and ‘as-milled HfO₂’.

Figure 2 depicts a schematic drawing and a photo of the DLD process used in this study. Laser deposition of the MAed powder was conducted on the Fe-14Cr-3W stainless
steel substrate using a continuous wave (CW) diode laser with a maximum power of 250 W (PF-1500F model; HBL Co.). The laser deposition machine was equipped with a coaxial powder feeder system controlled in real time. ODS powder particles were delivered to the molten pool through the coaxial powder nozzle with an ultrasonic vibration system [18]. A MAed powder that was sieved with a mesh with a nominal aperture of 100 mm was used for the DLD process. During the DLD process, Ar carrier gas with a rate of 10 liter/min was flowed directly into the laser focused area in order to prevent oxidation. The lens system focused the beam to a 250 μm diameter on the working plane with a hatch distance of 100 μm. A laser power of 150 W and a scan speed of 3 mm/s were selected for this work. After the laser deposition, the samples were post-annealed at 1100 °C for 1 hour under a vacuum condition of 10⁻⁶ torr. Detailed descriptions of the experiment can be found elsewhere [18].

To observe the cross-section of the deposition layer, we used a JSM-7001F SEM. The deposition layers were mounted with epoxy resin, polished, and etched with a 3:1:1 ratio of hydrochloric, nitric and acetic acid for 15 s. The detailed microstructures of the ferrite matrix and NPs were examined using a Cs-corrected scanning transmission electron microscopy (STEM, JEM-ARM200F instrument) operated at 200 kV. An energy dispersive X-ray spectroscope (EDS) was utilized in the STEM mode to determine the concentration ratio of Y and Ti in the particles. TEM samples were prepared by lifting out the deposition layer utilizing a focused ion beam (FIB) (FEI, Helios Nano-Lab 600). The FIB sampling was obtained from the middle of the deposition layer.

3. RESULTS

Figure 3 presents a macro photo of a sample after the laser beam scanning. The surface of the deposition layer was slightly rough. The length and width of the deposition layers were 30 and 1.5 mm, respectively. Figure 4(a) and 4(b) are the cross-sectional images of the deposited layers of ‘as-milled Y₂O₃’ and ‘pre-annealed Y₂O₃’, respectively. Both deposition layers showed significant pore formations, which were made up of micropores and larger pores. The pore distribution on the deposition layer of the ‘pre-annealed Y₂O₃’ was slightly higher than that of the ‘as-milled Y₂O₃’. Figure 4(c) and 4(d) display the SEM cross sectional images of the deposited layers of the ODS steel with HfO₂ dispersoid, with 4(c) and 4(d) representing the ‘as-milled HfO₂’ and the ‘pre-annealed HfO₂’, respectively. The ‘as-milled HfO₂’ showed very few pores as compared to the ‘pre-annealed HfO₂’ which showed a combination of small and large pores. The pore formation observed in all the deposition layers is attributed to the gas that remained during the melting of the powders in the DLD process. Because MAed powders...
Inherently contain porosities, it is very difficult to avoid porosity formation.

Figure 5 displays magnified SEM images of the deposition layers, revealing grain sizes and particle distributions. Figure 5(a) depicts the microstructure of the ‘as-milled Y2O3’ of the Y2O3 dispersed ODS steel. The grains appear to be coarse with a grain size of approximately 28 µm. There were a few nanometre sized particles dispersed within the matrix.

Figure 5(b) displays the microstructure of the pre-annealed condition of the Y2O3 dispersed ODS steel. It also showed coarser grains, with a grain size of approximately 38 µm. For the particle distribution, there was a relatively higher number density of dispersed nanometre sized particles within the matrix, compared to the ‘as-milled Y2O3’.

The deposition layers of the HfO2 dispersed ODS steels also exhibited results similar to those of the Y2O3 with regards to the nature of the observed grains. The grain size of the ‘as-milled HfO2’ was approximately 88 µm and there were many nanometre sized particles dispersed within the microstructure, as shown in Fig. 5(c). For the ‘pre-annealed HfO2’ shown in Fig. 5(d), the grains also appeared coarser, with a grain size of approximately 140 µm.

For the particle distribution, there were only a few traces of nanometre sized particles dispersed in the matrix. From the SEM analyses, it was observed that in the as-milled conditions of both the Y2O3 and the HfO2 dispersed ODS steels, the grain size of the ‘as-milled HfO2’ deposition layer was coarser than that of the ‘as-milled’ deposition layer.

Moreover, regarding the particle distribution in the deposition layers, the HfO2 dispersed ODS steel exhibited a higher number density of NPs compared to the Y2O3 dispersed ODS steel. With regards to the pre-annealed conditions, the grain size of the deposition layer of the ‘pre-annealed HfO2’ was also coarser than the ‘pre-annealed Y2O3’. Furthermore, for the particle distribution in the deposition layers, the Y2O3 dispersed ODS steel had a higher number density of NPs than the HfO2 dispersed ODS steel.

In a nutshell, the ‘as-milled HfO2’ deposition layer of the HfO2 dispersed ODS steel had the highest number density of NPs. Due to the resolution limit of the SEM, the nature of the particles could not be analysed, and therefore TEM analysis was necessary.

Another interesting observation from the SEM results is that the grain sizes of the deposition layers appeared to be unusually coarse, compared with those in conventional bulk ODS steels. As a result, it was necessary to confirm the grains observed in the SEM results by TEM analysis.

Figure 6 displays high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images of ‘as-milled Y2O3’ and ‘as-milled HfO2’. In contrast to the SEM images, the TEM observation revealed a fine nano-grained structure as well as coarse grained regions. Elongated grains with an average grain size of ~50 nm had...
Fig. 7. (a,b) HAADF-STEM images at the nano-grained region of the ‘as-milled Y$_2$O$_3$’ deposition layer and (c) a histogram showing the grain size distribution. The inset in (b) depicts a SAED pattern taken from the matrix.

Fig. 8. (a,b) HAADF-STEM images at the nano-grained region of the ‘as-milled HfO$_2$’ deposition layer and (c) a histogram showing the grain size distribution. The inset in (b) depicts a SAED pattern taken from the matrix.

grown perpendicular to the deposition direction.

Figures 7(a,b) display magnified HAADF-STEM images of the nano-grained regions of the ‘as-milled Y$_2$O$_3$’. The very fine grain size can be clearly visualized. Figure 7(c) depicts a histogram of the corresponding grain size distribution. There were both fine and coarse grains observed. The average grain sizes of the fine and coarse grains were approximately 48 and 119 nm, respectively. The selected area electron diffraction (SAED) pattern shown in the inset in Fig. 7(b) displays a typical ring pattern, indicating high angle grain boundaries. The mechanism for this disparity in grain size is not yet understood and further work needs to be done to investigate the reason. A probable reason is that, during the laser melting, some part of the powders experienced incomplete melting and therefore remained in the solid state. A more detailed analysis is given in the Discussion section.

Moreover, NPs were not clearly observed in the microstructure, which was different from the SEM results, where small particles were observed but could not be analyzed.

Figure 8(a,b) and 8(c) display HAADF-STEM images of the nano-grained regions of the ‘as-milled HfO$_2$’ and a histogram of the corresponding grain size distribution, respectively. In contrast to the deposition layer of the ‘as-milled Y$_2$O$_3$’ ODS steel, grain sizes were coarser with the average grain size of approximately 203 nm. NPs were also clearly not observed in the microstructure, like the TEM results of the ‘as-milled Y$_2$O$_3$’ dispersed ODS steel. The absence of NPs in the microstructures in the TEM results appears to contradict the results from the SEM analyses, where nanometre-sized particles were observed in all the deposition layers.

From the TEM results, the average nano grain size of the ‘as-milled HfO$_2$’ was coarser than the ‘as-milled Y$_2$O$_3$’ deposition layer. Figure 9 demonstrates the dislocation structure at the nano-grained region and coarse-grained
Fig. 9. TEM images of the ‘as-milled HfO₂’ showing dislocation structure at (a) nano-grained region and (b) coarse-grained region. Arrows indicate the locations of dislocation bowing.

Figure 10 presents the results of the Vickers micro-hardness measurements for the deposition layers. The average micro-hardness value of the substrate was approximately 155 HV, with 265 and 203 HV being the average micro-hardness values of the deposition layers of the ‘as-milled Y₂O₃’ and the ‘pre-annealed Y₂O₃’ of the Y₂O₃ dispersed ODS steel, respectively. For the HfO₂ dispersed ODS steel, the average micro-hardness values for the ‘as-milled HfO₂’ and the pre-annealed HfO₂ were 214 and 187 HV respectively.

From the micro-hardness results it can be seen that the deposited layers of the Y₂O₃ dispersed ODS steel had higher micro-hardness compared to the HfO₂ dispersed ODS steel. Moreover, the micro-hardness of both the ‘as-milled Y₂O₃’ and the ‘as-milled HfO₂’ were higher than the pre-annealed conditions for both the Y₂O₃ and HfO₂ dispersed ODS steels.

4. DISCUSSION

In bulk ODS steels, the grain sizes are usually very fine, below 1 μm, even after longer annealing at high temperatures. This is because the high number density of oxide NPs effectively pin the movement of grain boundaries. A previous work by Nagini et al. [18], investigated the influence of high energy ball milling on the microstructure and the mechanical properties of a 9Cr ODS steel. The average grain sizes of the bulk ODS steels ODS1, ODS2, ODS3, and ODS4 (representing ODS steels milled for 1, 2, 3 and 4 hours respectively) after extrusion and annealing heat treatment were 0.84, 0.67, 0.68, and 0.63 μm, respectively. The average sizes and number densities of the dispersoids of the ODS1, ODS2, ODS3 and ODS4 were 16, 12, 8, and 5 nm and 2.0 × 10²³, 5.2 × 10²³, 3.3 × 10²³, and 6.0 × 10²³ m⁻³, respectively. Shen et al. [19] reported average grain size values in the range of 1-8 μm for the bulk 12Cr ODS steel produced. They reported the average size and the number density of the dispersoids to be 3.5 ± 0.7 nm and 1.3 × 10²³ m⁻³, respectively.

In the present work, the grain sizes of the ODS steels from the SEM analyses appeared to be unusually very coarse, as compared to the previously reported values of bulk ODS steels, as presented. It is possible that the observed grain boundaries in the SEM analyses are from the initial powder particle boundaries, while the grain boundaries observed in the TEM analysis (Fig. 6 through 8) are from the recrystallized grain boundaries. The discrepancy between the SEM and TEM observations is thought to be due to ineffective etching, which was not able to adequately etch the grain boundaries of the nano-sized grains. As a result, the nano-grained region was not clearly visualized during the SEM observation.

In Fig. 5, it was demonstrated that the pre-annealed conditions of both the Y₂O₃ and HfO₂ deposition layers...
revealed relatively coarser grains than the as-milled conditions. In the previous work [12], the NPs were retained after the laser melting process although the particle sizes were relatively coarser than the particle sizes of conventional bulk ODS steels. During MA, \( \text{Y}_2\text{O}_3 \) or \( \text{HfO}_2 \) is dissociated into yttrium and oxygen, or hafnium and oxygen, respectively [20]. The pre-annealing treatment at 1100 °C induces the nucleation and growth of complex NPs in the form of Y-Ti-O or Hf-Ti-O. Because the melting points of the NPs are much higher than the steel matrix, the NPs do not dissolve into the melt but rather diffuse through the melt and grow during the laser melting process.

The grown NPs are then easy to move and become highly buoyant in the melt due to the Marangoni effect [21], which results in the coarsening or removal of the NPs. This subsequently results in the coarsening of the grains, and a resulting decrease in hardness.

In contrast, in the as-milled state, the yttrium and hafnium remained in the dissociated state in the steel powder. In the liquid state during the laser melting, it was difficult for the yttrium and hafnium elements to recombine with the oxygen or titanium, and they were retained as solute elements in the melt. The yttrium or hafnium oxide then precipitated out as NPs during the post annealing stage. The NPs that emerged after the post annealing stage were very fine, below a few nanometers, and were difficult to observe using the normal TEM technique. The high number density of NPs were very effective in maintaining a fine grain size.

Figures 6 through 8 showed that the middle section of the deposition layers contained a nano-scale-grained region, which is an unusual microstructure. As has been already mentioned in the Results section, the mechanism for this unique microstructure formation is not clearly understood. One plausible assumption is that, during the laser melting process, some part of the powders was not completely melted, and therefore a solid state microstructure was retained. However, there is a discrepancy between the experimental results and this assumption. If the nano-grain size was inherited from the as-milled ODS powder before DLD, the average nano grain sizes of the ‘as-milled \( \text{Y}_2\text{O}_3 \)’ and the ‘as-milled \( \text{HfO}_2 \)’ should be similar. However, the ‘as-milled \( \text{Y}_2\text{O}_3 \)’ exhibited much finer grain size. In addition to that, the average grain size of the nano-grained region was even smaller than the average grain size of the as-milled ODS powder (10 nm in width and 300 nm in length) reported in literature [20].

In order to investigate the origin of the nano-grain formation, EDS analysis was performed on both the nano-grained region and the coarse-grained region of the ‘as-milled \( \text{Y}_2\text{O}_3 \)’. There was no difference in the composition level of Fe, Cr, W, and Ti between the two regions. However, the content of some minor elements, of O and refractory elements, were 3.5 at% higher in the nano-grained region. The higher O level implies the presence of \( \text{Y}_2\text{O}_3 \) or \( \text{HfO}_2 \) which can pin grain boundary movement, although the oxides were not well visualized by the TEM analyses. Also, refractory elements are well known to refine grain structure [22]. The minor elements are believed to have come from the milling media or the environment during the severe high speed milling.

We conducted another extra laser deposition process with an ODS powder based on 410 L. A similar laser deposition process was applied with same DLD machine, except using a faster scanning speed of 8 mm/s. In the extra experiment, a horizontal attritor milling instead of a high speed planetary milling was used. After DLD, complete powder melting was found, in spite of the faster scanning speed.

Figure 11 displays TEM images of the microstructure of the fabricated deposition layer using the 410 L stainless steel powder. In this case, the mean grain sizes of the deposition layers were in the range of 2–10 μm, which is quite different.
Based on this result, we propose that the unique nano-grained structure might be due to some chemical compositional effect, due to a combination with unidentified complex mechanisms. Simple incomplete melting or the rapid solidification mechanisms cannot account for this phenomenon. Therefore, further studies are necessary in the future.

5. CONCLUSIONS

The feasibility of using HfO₂ as a dispersoid in the AM process using the DLD technique was studied and compared to the use of Y₂O₃. The effect of a pre-annealing treatment, which is normally performed to stabilize complex oxide particles during the conventional powder metallurgy process, was also investigated. A summary of the findings and conclusions are given below.

The SEM analyses of the deposition layers produced using the DLD process revealed unusually coarse deposition layers with sizes of several micrometres for both the HfO₂ and Y₂O₃ dispersed ODS steel, in both the as-milled and the pre-annealed conditions.

The deposited layers of the pre-annealed conditions of both Y₂O₃ and HfO₂ dispersed ODS steels showed relatively coarser grains than the as-milled conditions.

The HfO₂ dispersed ODS steel had relatively coarser grains than the Y₂O₃ dispersed ODS steel in both the as-milled and the pre-annealed conditions.

Nanometre sized dispersed particles were observed in the deposited layers of both the Y₂O₃ and HfO₂ dispersed ODS steels. However, their number densities were far lower compared to conventional bulk ODS steels.

In the middle of the deposited layer of the ‘as-milled Y₂O₃’ and the ‘as-milled HfO₂’ dispersed ODS steels, unusual nano-grained structures with grain size distributions between 50 ~ 200 nm were observed.

The average micro-hardness values of HfO₂ and Y₂O₃ dispersed ODS steels in both the as-milled and the pre-annealed conditions were higher than that of the substrate. The micro-hardness observed for the as-milled conditions were higher than that of the pre-annealed conditions for both the Y₂O₃ and HfO₂ dispersed ODS steels. Furthermore, the Y₂O₃ dispersed ODS steel had higher micro-hardness than the HfO₂ dispersed ODS steel in both the as-milled and the pre-annealed conditions.

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REFERENCES