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SURFACE and INTERFACE ANALYSIS WILEY

Surface modification of Ti-6Al-4V powder during recycling in EBM process

Yu Cao[1] | Mats Delin[2] | Fredrik Kullenberg[2] | Lars Nyborg[1]

[1]Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg, Sweden

[2]GKN Aerospace Engine Systems, Trollhättan, Sweden

Correspondence
Yu Cao, Department of Industrial and Materials Science, Chalmers University of Technology, Gothenburg, Sweden.
Email: yu.cao@chalmers.se

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Electron beam melting is an additive manufacturing technology in vacuum that suits Ti-6Al-4V parts, which has a high affinity with oxygen. Since the high cost of the feedstock powder, the un-melted powder is often recycled in the subsequent process. In this study, the influence of powder reuse on the surface characteristics of Ti-6Al-4V powder is examined using a variety of technology including scanning electron microscopy, X-ray photoelectron spectroscopy, and Auger electron spectroscopy. The modification of surface morphology and chemistry either generally or locally are revealed and discussed, which helps the creation of powder recycling strategy. Compared with fresh virgin powder, "worn" and rougher powder particles are observed after recycling. Meanwhile, the average oxide thickness is slightly increased, and less Al enrichment was found at the surface. Locally varied chemistry/oxide thickness on different powder particles or different location on the same particle is observed.

KEYWORDS
AES, electron beam melting (EBM), recycling, Ti-6Al-4V, XPS

1 | INTRODUCTION

Additive manufacturing (AM) is the general term for all manufacturing techniques where the component is built by adding material layer by layer from a CAD (computer-aided design) model. AM allows manufacturing of complex products with near-net shape such as structural parts with internal features and complex internal cooling channels. AM has an ability to join the same materials or different materials together. The design freedom is very high. This enables faster product development, short development cycles, lighter products, and more efficient use of the material. There are many different additive manufacturing techniques available. Electron beam melting (EBM), developed by the Swedish company Arcam AB, is a core AM technology for building parts using high-energy electron beam, by which a large fraction of thermal energy is released to heat, sinter, and melt the powder material. EBM works in vacuum environment, which lowers the risk of oxidation, being a good choice for material with high affinity to oxygen. It involves the preheating of the powder with build temperature of $\sim$ 600–750°C before melting, which reduces the temperature gradient and thus decreases the residual stresses.

Titanium is a relatively light metal with density of 4.51 g/cm^3, which is significantly lower than those of commonly utilized engineering metal Fe, Ni, and Cu (7.87–8.96 g/cm^3). Titanium alloys are well known as material for the aerospace industrial since 1940s. The most popular Ti alloy is Ti-6Al-4V, a $\alpha + \beta$ alloy containing 6 wt% Al and 4 wt% V. More than 50% of all alloys in use today are of this composition. Titanium alloys have high strength to weight ratio, making them optimum materials for components such as airframes, blades, and disks in jet engine in the aerospace industry. Due to low density, good corrosion resistance, and biocompatibility, they are well suited for medical applications as body implants, e.g., artificial hip joints. Titanium alloys have also found wide range of application in energy, automotive, sports, and customer goods industry. The conventional manufacturing relies on casting, rolling, forging, and machining. The

EBM is a preferred AM technique for fabricating Ti alloy parts considering high affinity of Ti to oxygen. The microstructure of as-built Ti-6Al-4V is generally fine lamellar α + β with both colony and basketweave morphology. Anisotropic and graded microstructure[1] has been observed. In case of short builds, thin-wall structures, or net structures, the presence of α′ martensite was also reported. Post heat treatments below the transus temperature induce coarser α lamellae when cooling slowly with some globular morphology.[2]

In the powder-bed process, only a limited portion of powder is melted and solidified in an EBM process. Unmelted powder is intended to be reused due to the high powder cost. In the real industrial practice, hundreds of recycling steps are often performed, and building may have variable duration. Sieving operation is often conducted. Repeated heating and cooling in vacuum during an EBM process may modify the un-melted metal powder gradually in terms of shape, size distribution, surface morphology, and chemistry. The objective of this study is the influence of powder reuse on the surface chemistry and morphology.

2 | EXPERIMENTAL

Commercial Ti-6Al-4V powder produced by plasma atomization production was used in this investigation. More than 90 wt% has particle size between 45 and 106 μm. After each EBM building process using Q10+ system (Arcam EBM, Sweden), powder was sieved and reintroduced into a subsequent production line without any addition of virgin supply. Both the virgin powder and powders recycled for 5 and 10 times were analyzed.

PHI 5000 VersaProbe III scanning X-ray photoelectron spectroscopy (XPS) microprobe was used with monochromated Al Kα radiation (1486.6 eV) to investigate the chemistry including compositions and chemical states at powder surface. Spectra were recorded with a 100-μm X-ray beam size and pass energy of 140 and 26 eV for surveys and high-resolution measurements, respectively. Area mode was used with the selected size of 400 × 400 um covering more than ~50 powder particles. The measurement was repeated at least twice on two specimens. This means XPS results shown in this paper provided the average chemical information of the powders. The

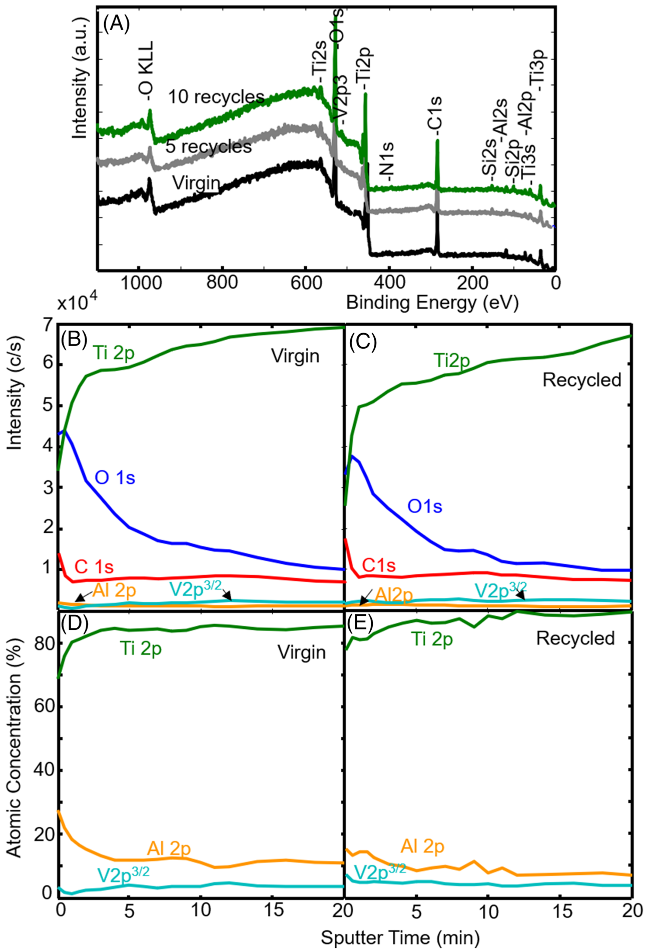


FIGURE 2 X-ray photoelectron spectroscopy survey spectra from the powders (A); X-ray photoelectron spectroscopy depth profiles (B, C) and cation profiles (D, E) from virgin powder (B, D) and powders recycled for 5 times (C, E). The etch rate is 24.8 Å/min for Ta_2O_5 with known oxide thickness

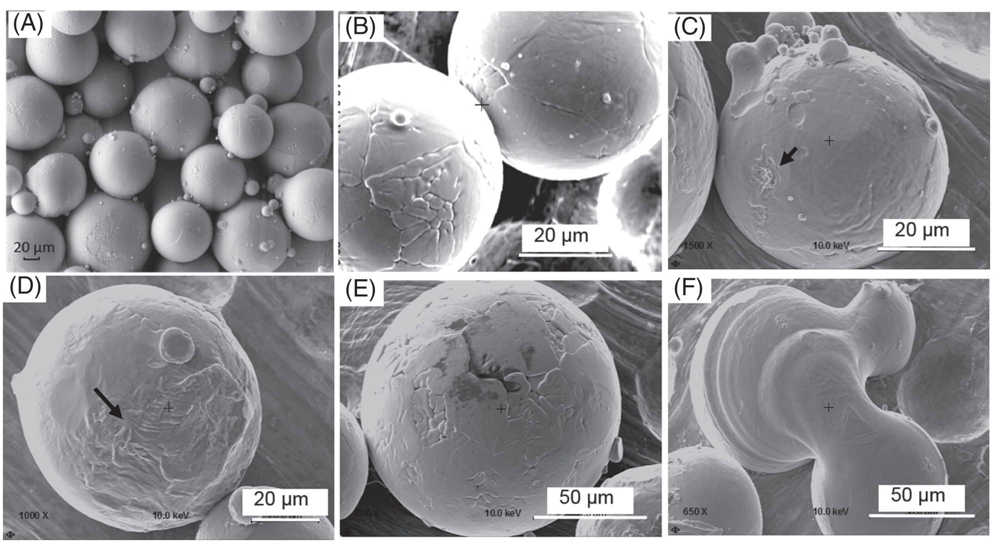


FIGURE 1 Scanning electron microscopy images of the virgin powder (A, B) and powders recycled for 5 (C, D) and 10 (E, F) times

compositions of local features on the powder surface were determined using a PHI 700 Scanning Auger electron spectroscopy (AES). The electron accelerating voltage was 10 kV, and the beam current was 10 nA. Image was registered frequently in AES to ensure the data were acquired at the location intended. The oxide thickness is defined as the depth where the intensity of oxygen decreases half by means of successive XPS/AES analyses and argon ion etchings over an area of 3 × 3 mm with ion beam accelerating voltage of 2.0 kV. Standard sensitivity factors provided by the PHI Multipak software were used to retrieve the apparent compositions. The nominal etch rate was calibrated by using Ta_2O_5/Ta samples with well-known oxide thickness. The morphology of the virgin and reused powder was investigated by means of a LEO Gemini 1550 scanning electron microscope (SEM) and the microscope attached in AES.

3 | RESULTS

Figure 1 gives the SEM images from the powder studied. Virgin powder was highly spherical with some satellites and small particles (Figure 1A). In general, it possesses relatively smooth surface with equiaxed structures (Figure 1B). Sometimes acicular martensite was observed. Occasionally, elongated or broken particles could be detected. After recycling, it seems that there was fewer satellite. Most particles maintained spherical shape but less smooth. Roughening of the surface was often observed, as indicated by the arrows in Figures 1C and 1D. This might be related to the local oxidation or partial melting. Few aggregates could be encountered, as shown in the top of Figure 1C. Particles might be sintered due to melting (Figure 1F). It should be mentioned that features similar to the virgin powder were also seen from both recycled powders. Theses powders were less affected by the EBM process, though the particles might be contaminated occasionally (Figure 1E).

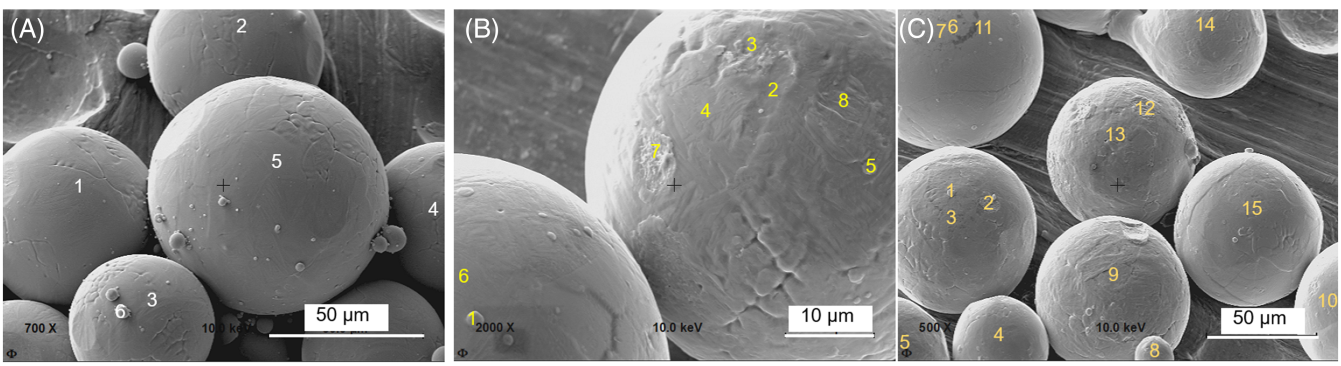
TABLE 1 XPS quantification of cation and oxide thickness determined by XPS at surface

	Ti at% (wt%)	Al at% (wt%)	V at% (wt%)	Oxide thickness by XPS (nm)
Virgin	70.7 (79.5)	27.6 (17.5)	1.8 (3.0)	6.5
5 recycles	79.3 (84.4)	14.6 (8.7)	6.1 (6.9)	7.35
10 recycles	78.0 (82.9)	15.9 (9.6)	6.1 (7.0)	7.54

XPS survey spectra from the powders studied are shown in Figure 2A. On the surface of all samples, O, C, Ti, Al, V, and a small amount of N were observed. Titanium oxide containing some Al and V was dominant. Part of N was in the form of nitride. A few Si was detected after recycling, which was believed from the EBM process. When considering only Ti, V, and Al, the cation composition at the surface is shown in Table 1. Compared with the nominal composition of the powder, higher Al and slightly lower V were detected at the surface of the virgin powder. Recycling reduced the concentration of Al, while V concentration was increased a little at the surface.

By etching with argon ions, depth profiles were obtained, as exhibited in Figures 2B and 2C. It should be noticed that the spherical shape of the powder and the interaction of argon ion beam with Ti6Al4V made C and O be extended in the profiles even far away from the surface. One observation was, in the presence of C, titanium carbide was formed during sputtering. The purpose of depth profiling in this study was to compare the average oxide thickness under different conditions. We simply defined it as the depth where the intensity of oxygen decreased half. The powder shape was not accounted for here. It should be viewed as approximate on an absolute scale. However, the differences between the powders under different condition can be consistently depicted. As revealed in Table 1, the overall oxide became thicker after recycling. The oxide thickness determined was 6.5 nm for virgin powder and 7.35 nm and 7.54 nm for powders reused for 5 times and 10 times, respectively. This was consistent with the result from Tang et al.[3], who reported a small but steady increase of O concentration in the powder as the build number was increased.

In order to examine the distribution of metal elements in depth, XPS cation profiles from the virgin and recycled powders were obtained, as shown in Figures 2D and 2E. In the virgin state, enrichment



Oxide thickness (nm)

(A)			(B)				(C)				
1: 6.4	2: 6.2	3: 4.5	1: 5.5	2: 6.6	3: 7.1	4: 5.9	1: 6.7	2: H*	3: 8.6	4: 6.5	5: 6.2
4: 4.1	5: 4.9	6: 4.7	5: 6.4	6: 6.0	7: 8.7	8: 5.9	6: 8.6	7: 11.8	8: 7.6	9: 12.1	10: 17.8
							11: H*	12: 7.1	13: 8.6	14: 10.0	15: 8.8

*: H means oxide thickness larger than thatt can be measured in the current experimental condition

FIGURE 3 Oxide thickness at different locations measured by Auger electron spectroscopy for virgin powder (A) and powders recycled for 5 (B) and 10 (C) times. The etch rate is 25.6 Å/min for Ta_2O_5 with known oxide thickness of Al was clearly seen in the surface region. The nominal composition was reached at a depth of ~15 nm (Figure 2D). The enrichment of Al was significantly reduced after recycling (Figure 2E). Meanwhile, V at the surface might be slightly higher than the nominal concentration.

Thanks to the high lateral resolution, AES is a wonderful tool to investigate the local surface chemistry. Figure 3 gives the oxide thickness at varied locations of different powders. For virgin powder (Figure 3A), the oxide thickness was between 4.1 and 6.4 nm with an average value of 5.1 nm. It was slightly smaller than the value from XPS because the location was selected to avoid the shadowing effect in AES analysis. As a general trend, oxide became thicker after recycling (Figures 3B and 3C). This was consistent with the results from XPS. However, surface oxide became less homogeneous and local thicker oxide was found. For example, points 3 and 7 in Figure 3B (recycled for 5 times) having local rough feature possessed significantly thicker oxide. Figure 4 exhibits the depth profiles of points 4 and 7 in Figure 3B. They differed in both oxide thickness and Al concentration. Compared with location 4 (Figure 4A) which was smooth, the oxygen profile of point 7 became less steep (Figure 4B), indicating increased oxide thickness. Meanwhile, the surface was more contaminated by carbon. Considerably more Al was detected in this local rougher place (Figure 4D compared with Figure 4C).

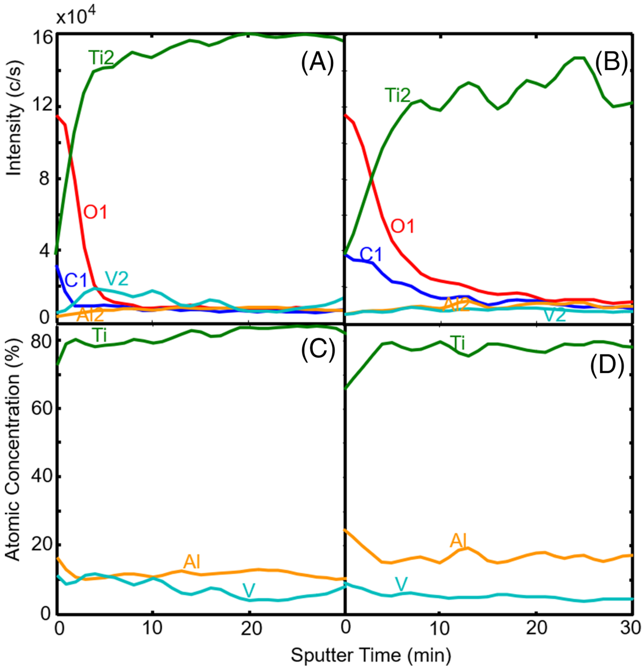


FIGURE 4 Auger electron spectroscopy depth profiles (A, B) and cation profiles (C, D) from the powder recycled for 5 times at location 4 (A, C) and 7 (B, D) in Figure 3B. The etch rate is 25.6 Å/min for Ta_2O_5 with known oxide thickness

The unevenness was even obvious for powder recycled for 10 times, as shown in Figure 3C. It should be mentioned that the oxide thickness obtained was dependent on the thermal history of the powder particles selected. Figure 5A is a local area found on the surface of the powder recycled for 10 times. Interestingly, AES analysis (Figure 5B) indicated that point 2 was almost pure Al oxide, while point 1 also contained some Fe, which was a common impurity in Ti-6Al-4V.

4 | DISCUSSION

Electron beam melting is a process performed in a vacuum chamber with a base pressure of ~ 10^{-4} mbar or better throughout the entire

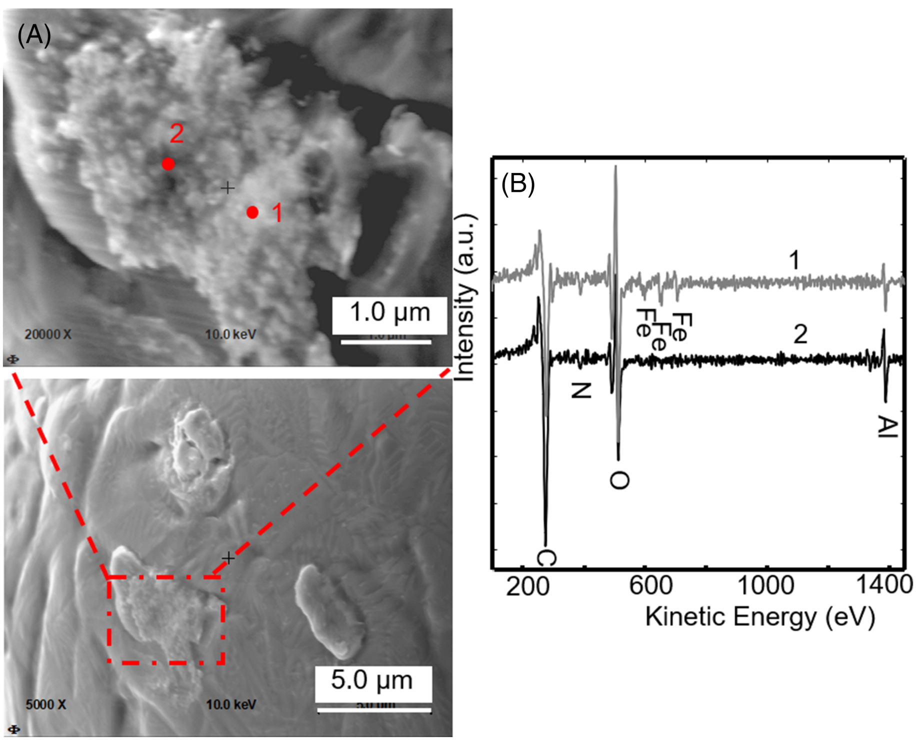


FIGURE 5 A local area (A) on the surface of the powder recycled for 10 times and the corresponding Auger electron spectroscopy spectra (B)

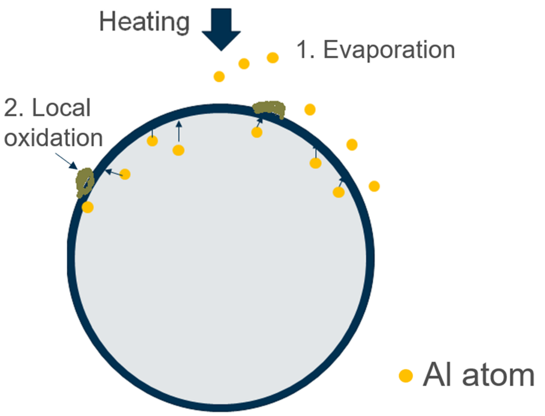


FIGURE 6 Schematic illustration of the event related to Al atoms in an electron beam melting process

build cycle, combined with a high build temperature of ~ 600–750°C. The temperature in the molten pool is estimated to be between 1900 and 2700°C.[4] Un-melted powders thus experience repeated heating and cooling. Aluminum has higher vapor pressure than Ti, and V has the lowest. The estimated vapor pressure for Al is 6.5 mbar at 2000 K and 0.01 mbar at 1500 K. The evaporation temperature is expected to be even lower in vacuum.[5] It is indeed a natural process that Al having high vapor pressure evaporates during the EBM process, leading to reduced Al concentration at the surface, as revealed in Figure 2C. Considering Al being a principal strengthening element of the α-matrix, local depletion is expected to affect the mechanical properties. On the other hand, according to Ellingham diagram, Al has the highest affinity with O compared with Ti and V. Though EBM is performed in the vacuum, some traces of oxygen always exist. High affinity with O provides the driving force for the diffusion of Al atoms towards the surface. As a result, local oxidation is observed, forming oxide with increased Al concentration. It is believed that increasing number of recycling makes more local oxidation. In the extreme case, Al dominant oxide can be formed at the surface, as confirmed in Figure 5. Figure 6 schematically illustrated these two processes, i.e., (a) evaporation of Al due to its high vapor pressure, leading to lower Al concentration at the surface, and (b) preferential oxidation of Al owing to its high affinity with oxygen, giving rise to local oxidation and formation of Al-enriched oxide. Iron is a common impurity in Ti-6Al-4V. Hematite has the same crystal structure (Hexagonal scalenohedral) as Al_2O_3. It is likely that initially formed Fe_2O_3 has an effect to promote the formation of Al_2O_3, as implied in Figure 5. Yuri Kitajima et al[6] suggested that the formation of an oxide scale having the same structure provides a nucleation site for precipitation or formation of Al oxide.

It is well known that O has large solubility in both α and β, especially in α. Oxygen pick-up and dissolution are also possible during powder recycling, especially at elevated temperatures. Oxygen is a strong α stabilizer and in principle provides interstitial hardening with lowered ductility. Such chemical composition change is expected to affect the microstructure and consequently the properties locally.

5 | CONCLUSIONS

In this study, the influence of powder reuse on the surface characteristics of Ti-6Al- 4V powder has been examined. Titanium oxide is dominant at the surface in general. Surface roughening, particle sintering, and partial melting are observed in the recycled powder. Averagely, oxide layer becomes thicker. The overall Al detected at the surface of the reused powder is less, probably due to the evaporation. On the other hand, localized oxidation with increased Al enrichment occurs owing to the high affinity of Al with oxygen. As a result, locally varied chemistry/oxide thickness on different powder particles or at different location on the same particle after recycling are found. This unevenness increases with recycling.

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ORCID

Yu Cao https://orcid.org/0000-0002-1965-5854

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