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Superelasticity in micro-scale shape memory ceramic particles

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ABSTRACT

Shape memory ceramics that exhibit repeatable superelastic deformation are of considerable significance for possible energy damping and micro-actuation applications, and the present work aims to further establish the structural conditions required to avoid fracture in these brittle materials. Spray dried micro-scale superelastic ceramic particles with a variety of grain structures were produced, ranging from single crystal to oligocrystal to polycrystalline particles. Micro-compression experiments showed that whereas polycrystalline samples fracture upon loading, oligocrystal and single crystal particles can exhibit cyclic superelasticity, the latter particles achieving highly reproducible superelasticity to over one hundred cycles with particle compressions up to 3.8% and dissipated energy up to 20-40 MJ/m³ per cycle. The mechanisms of structural evolution and fracture during cyclic loading are also explored.

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Introduction

Zirconia based shape memory ceramics (SMCs) are a unique family of smart materials with many potential applications in sensing, actuation, and mechanical energy damping [1,2,3,4,5] thanks to a reversible thermoelastic martensitic transformation from a high temperature tetragonal phase (referred to as austenite in the context of shape memory materials) to a low-temperature monoclinic phase (referred to as martensite) [6]. When these ceramics are in the high temperature phase, the transformation can be triggered through shearing of the austenite phase with applied stress, giving rise to a large shear strain as the lattice transforms to martensite. This crystallographic transformation strain can be fully recovered by releasing the stress to induce reverse transformation, leading to the moniker ‘superelasticity’ [7]. An early observation of superelasticity in zirconia ceramics was made by Reyes-Morel *et al.* [8,9] who reported that ceria stabilized tetragonal zirconia polycrystalline (Ce-TZP) ceramics exhibited superelasticity with a stress-induced transformation strain of ~0.5-1.0%. However, this strain is far below the full transformation strain of ~8%, and the superelastic behavior could only be repeated for 5-6 loading cycles before the samples failed due to intergranular cracking [8].

The cracking problem in superelastic SMCs originates at least in part from the large mismatch stresses accumulated between neighbouring grains with different crystal orientations as they each attempt to undergo a transformation that is crystallographically constrained and incommensurate between them. In our recent work [10,11], we have shown how this cracking problem can be mitigated by reducing the sample size so that it is on the order of the grain size, thereby creating a single crystal or oligocrystal structure that has a high free surface area and few grain boundaries, so as to minimize the transformation mismatch between different grains. In that work, micro- or nano-pillars with such structural features were machined by focused ion beam (FIB) milling and exhibited enhanced superelastic cycling capabilities (up to 50 cycles) and large stress-induced transformation strains of at least several percent [10].

Whereas micro- or nano- scale pillars of SMCs have provided critical proof-of-concept data, it is of interest to explore other oligocrystalline SMC form factors that are conducive to scaled-up production. It is the purpose of the present paper to consider oligocrystalline SMCs in the form of isolated spherical particles, which can be mass produced by spray drying [12]. Specifically, we explore a series of SMC particles $\sim 1\text{-}6\ \mu\text{m}$ in size, straddling the average grain size of $\sim 1.7\ \mu\text{m}$ and therefore sampling a range of oligocrystalline to single-crystal states. We identify structural conditions under which completely recoverable superelastic behaviour is achievable in the SMC particles, including multi-cycle loading beyond one hundred cycles. We also provide discussion on the failure mechanisms of SMCs based on transmission electron microscopy (TEM).

Materials and methods

SMC particles with a composition of 16%Ce-ZrO₂ were produced by spray drying a ceramic slurry with pressurized hot N₂ gas (Figure 1A). Firstly, polyvinyl alcohol binder with a molecular weight of $\sim 35,000$ was dissolved in hot water ($\sim 90^\circ\text{C}$) and subsequently cooled. Then a commercial dispersant, Darvan C-N (Vanderbilt Minerals, LLC), was added, followed by ceramic powders ZrO₂ and CeO₂ which were purchased from Guangdong Orient Zirconic and Sigma-Aldrich respectively, with particle sizes of $<100\text{nm}$. The aqueous slurry was then mixed by ball milling for 24 hours, and finally consisted of $\sim 2\ \text{wt.}\%$ PVA, $\sim 2\ \text{wt.}\%$ Darvan C-N, and $\sim 30\ \text{wt.}\%$ ceramic powder. The spray drier was a Büchi Mini Spray Drier B-290 with a nozzle tip diameter of 0.7 mm, with compressed N₂ gas at 100 psi. The inlet temperature was maintained at 135°C and the slurry feed rate was $\sim 30\ \text{ml/hr}$.

The as-prepared particles have a broad size distribution, ranging from $\sim 1\text{-}10\ \mu\text{m}$ (Figure 1D), which enables us to select particles of different sizes for subsequent studies. After annealing at 1500°C for 2 hours, the particles have an average grain size of $\sim 1.7\ \mu\text{m}$. They are

comprised solely of tetragonal phase (austenite) at room temperature, as confirmed by powder X-ray diffraction (XRD) (Figure 1E) and by high-resolution TEM (HRTEM) on a random particle (Figure 1F). The HRTEM image also shows that the particles have few lattice defects. The austenite and martensite finish temperatures were estimated to be $A_f \approx 0^\circ\text{C}$ and $M_f \approx -170^\circ\text{C}$ based on our prior work with this system and the measured compositions [10]. These particles are nominally suitable for superelasticity studies because at room temperature, they lie at a temperature above the austenite finish temperature, so applied stresses at room temperature can induce transformation to martensite, which should be subsequently recovered upon unloading.

The zirconia particles after annealing were separated from each other by ultrasonic processing in ethanol for 60 seconds and then coated on a quartz substrate (Figure 1B). The morphology of the particles was then observed by scanning electron microscopy (FEI Nova 600i Nanolab). Only those particles with spherical or near spherical shapes were selected for further study. The particles with diameters of $\sim 1\text{-}6\ \mu\text{m}$ exhibited a variety of grain structures, ranging from polycrystalline in the larger particles (i.e., more than about 10 grains, Figure 1G), oligocrystalline in medium-sized particles (approximate $\sim 2\text{-}8$ grains, Figure 1H), to single crystals at the smallest particle sizes (only one grain, Figure 1I). For selected particles, a circle of diameter of $20\ \mu\text{m}$ was etched around the particle using a focused ion beam (FIB) (FEI Nova 600i Nanolab). These circles served as fiducials to identify and test specific, isolated particles of interest.

Uniaxial micro-compression tests on the SMC particles were carried out using a Hysitron Triboindenter TI 950 equipped with a 60° conical tip with a flat end (the diameter of the flat, circular platen was $10\ \mu\text{m}$, much larger than any particle tested herein). The tip was carefully centered over each tested particle (Figure 1C). The loads applied were in the range of $\sim 0.5\text{ - }10\ \text{mN}$ and a fixed loading and unloading rate of $\sim 50\ \mu\text{N/s}$ was used throughout, with

no hold time at the maximum load. To perform many cycles of loading in a reproducible and comparable way, we separated the tests into segments in which 10 identical loading & unloading cycles were conducted with the specified maximum load and constant loading rate. Between the segments, a set-point 2 μN contact force was always maintained and contact with the specimen was never broken.

The cross-section of a particle subjected to 16 superelastic cycles was characterized by transmission electron microscopy (TEM, JEOL 2100F). The sample was prepared by using an in situ lift-out technique [13] in the FIB milling system mentioned earlier. To confirm the crystal phase of the particles after sintering at 1500°C for 2 hours, another particle was analyzed by HRTEM.

Superelasticity

We first tested dozens of particles with different degrees of polycrystallinity. Particle #1 (see Figure 1G) had a diameter of $\sim 4.2 \mu\text{m}$, and is an example of a polycrystalline structure, having more than 10 grains. Upon loading this particle in compression, we observed a concave-upward load-displacement response (Figure 2A), as expected for a Hertzian sphere-on-plate contact responding elastically [14]. This behaviour persisted to a load of about 3.5 mN, after which a series of displacement bursts were observed. These bursts might be associated with the martensitic transformation, with cracking, or with both, but at an ultimate load of 4.8 mN, the particle was crushed through multiple fracturing, as shown in Figure 2D.

We measured the load at the first apparent yield point (F_{yield}) from the load-displacement curve in Figure 2A. This point lies at the first departure from apparent elastic behaviour, and as such it can be analysed using elastic contact theory to estimate the stress levels present in the particle at the yield event. Figure 2E shows a model description of a particle compressed by a flat punch. According to Hertzian theory, the contact normal force F_e for elastic contact can be described by the following equation [15]:

$$F_e = \frac{2}{3} E^* \sqrt{R} s^3 \quad (1)$$

where, R is the radius of the particle before compression and s is the total displacement of the particle and flat plate at the contact point. E^* is the effective biaxial Young modulus of the paired contacting materials. While in principle E^* can be calculated from the known Young's moduli and Poisson ratios of the materials used in the experiment, the modulus of zirconia is highly anisotropic; without knowledge of the specific crystal orientations involved in a given test, the expected E^* can only be bounded to within >100 GPa, which is not useful for analysis. Accordingly, in what follows we treat E^* simply as a fitting parameter, the extraction of which permits estimation of the maximum contact stress (in compression), which lies in the center of the contact at point K in Figure 2E, and is given by [15,16]:

$$p_{max} = \sqrt[3]{\frac{3F_e E^{*2}}{2\pi^3 R^2}} \quad (2)$$

The martensitic transformation of zirconia is driven primarily by shear stress. So if the first displacement burst in the loading curves is taken to correspond to the first activation of the transformation, then the scale of the deviatoric stresses in the sample is physically relevant. The maximum shear stress for Hertzian loading occurs at a depth of about half of the contact radius ($0.5r_e$) beneath the contact point (point Z in Figure 2E) and is given by:

$$\tau_{max} = 0.30 p_{max} \quad (3)$$

By fitting Equation (1) to the loading curve of Particle #1, we attain a good match (see the dashed line in Figure 2A) and extract a fitted value of the contact modulus $E^* = 40.3$ GPa. The maximum shear stress at the first yield point is ~ 1.91 GPa according to Equations (2-3).

Particle #2 was ~ 3.5 μm in diameter, containing ~ 4 or 5 grains (Figure 1H). This corresponds to what can be termed an oligocrystalline structure, having more surface area than grain boundary area [17,18]. The load-displacement curve for this particle is shown in Figure 2B. Again, the loading curve fits nicely with the theoretical Hertz curve by using the contact

modulus $E^* = 124.5$ GPa, which indicates the particle has a nominal Hertzian elastic response followed by a yield event that has the appearance of a discontinuity, and several additional small displacement plateaus as noted by the arrows. It seems likely that these displacement bursts can be attributed to the martensitic phase transformation, because after achieving a load of 6.0 mN, the particle was unloaded and exhibited essentially perfect displacement recovery, including some discontinuities or bursts denoted by the arrows in the unloading curve in Figure 2B, suggestive of reverse transformation. The sample hence exhibits the characteristics of the superelastic effect [19]. The load which initiated the martensitic transformation (i.e. F_c in Figure 2B) is 4.3 mN. At this load, the maximum shear stress is ~ 3.05 GPa, which is much higher than that which led to yield and failure of particle #1. The dissipated energy for one superelastic cycle is estimated to be ~ 4.2 MJ/m³ based on the area enclosed by the load-displacement curve.

Particle #3 is an example of a single crystal particle ~ 1.6 μm in diameter. During loading, this particle also exhibited Hertzian elastic behaviour followed by apparently superelastic shape change (Figure 2C, $E^* = 91.9$ GPa from Hertz fitting) including large displacement bursts of ~ 30 nm in both the loading and unloading curves (noted by the arrows). From the width of the displacement plateau in Figure 2C, $d_{a \rightarrow m}$, the stress-induced normalized particle compression ($\varepsilon_{a \rightarrow m}$) can be estimated as [20]:

$$\varepsilon_{a \rightarrow m} = \frac{d_{a \rightarrow m}}{2R} \quad (4)$$

The transformation compression of Particle #3 can be estimated to be $\sim 1.9\%$, and evolved over a very short time (~ 12 ms). The load for initiating martensitic transformation (F_c) is 1.66 mN, at which the maximum shear stress is ~ 3.04 GPa. This stress level is also much higher than that attained in the polycrystalline particle #1 and the dissipated energy over the full loading cycle is ~ 38.3 MJ/m³.

The results presented above are typical of the many experiments that we have conducted, and clearly show the critical role of grain structure in determining the superelastic properties of the SMC particles. Polycrystalline particles fail to exhibit superelasticity, tend to develop permanent deformation (due mainly to cracks) and subsequently be crushed. This behaviour is similar to that seen in bulk polycrystalline SMCs [21,22] and generally associated with grain boundaries due to the local concentration of transformation mismatch stresses there [23]. Figure 2D shows polycrystalline particle #1 after crushing, with prominent intergranular cracking along the grain boundaries and triple junctions (denoted by arrows).

We have compressed dozens of particles in the manner described above, and analysed the maximum shear stress attained at the first departure from elasticity. As shown in Figure 3A, the maximum shear stresses reached in polycrystalline particles (~1.0 - 2.0 GPa) are generally low compared with those from single-crystal particles (~3.0 - 4.0 GPa). According to our previous studies, the critical transformation stress we have measured for micro-scale SMC pillars (diameter: 1 μm) is about 0.58 - 8.7 GPa in compression, which can be resolved to a shear stress of 0.29 - 4.35 GPa [24]. The range of these measurements is related to crystallographic orientation and the anisotropy of the transformation stress, and also exhibits a size dependence, rising in proportion to the size of the pillars [24]. For the pillars with diameters above about 2 μm , the critical shear transformation stress can be above 4.35 GPa [24]. The size effect on the transformation stress can also be explained from the thermodynamics of martensitic transformation [25,26]. For a single-crystal particle free from matrix constraint, the external applied energy for transformation ΔU_{ex} should at least meet the lower bound condition: $\Delta U_{ex} = \Delta G_c + \Delta U_s$, where ΔG_c is chemical free energy change between the phases, and ΔU_s is the surface energy change between them. With increasing particle diameter, the particles become polycrystal and each grain is increasingly constrained by surrounding grains. This adds a strain energy ΔU_{se} associated with the matrix constraint should that must also be overcome by the

external applied energy: $\Delta U_{ex} = \Delta G_c + \Delta U_{se} + \Delta U_s$. This results in a higher transformation stress for polycrystalline particles as compared with the smaller single crystal ones.

This can help explain the trend seen in Figure 3A, where the larger particles fracture at stresses below the transformation stress level seen in the pillars with diameters above about 2 μm (~ 4.35 GPa); the stresses needed to cause intergranular fracture are below the expected transformation stress level. For somewhat smaller particles with fewer grain boundaries, especially single-crystal particles, the stress levels more closely match one another, and transformation can occur at essentially the same load level that fracture sets on, or lower; in fact the added stress of the transformation mismatch likely contributes to fracture in those polycrystalline samples that fractured without sustaining apparent superelastic strain.

Oligocrystalline particles (refer to the particles with diameter 2.5 - 4 μm , Figure 3A) have fewer grain junctions and more stress-relieving free surface area, both of which decrease the geometrical constraints that lead to higher transformation stresses and crack formation. Therefore the particles can sustain higher shear stress at the yielding point, which we find to lie in the range ~ 2.0 - 3.0 GPa. These particles are therefore far more likely to attain the transformation stress level and survive superelastic cycling. For example, particle #2 was subjected to dozens of cycles of superelasticity while remaining almost intact (Figure 4A-B). However, as the martensitic transformation is anisotropic and such samples still have compatibility challenges among the various grains in the sample, the dissipated energy for one loading-unloading cycle is relatively low, at ~ 4 - 10 MJ/m³.

Single crystal particles have no grain boundaries; they cannot crack intergranularly and they routinely survive the transformation and show superelasticity (cf. Figure 2C). If overloaded they can still fail, but do so in a different manner from polycrystalline particles. Figure 3B shows a typical load-displacement curve of particle #4 obtained from one-time

loading to the point of crushing as an example. Generally, the particles will go through Hertzian elastic deformation (see the curve a-b in Figure 3B), deformation due to martensitic transformation (curve b-c) and then, if they are not unloaded, apparent plastic deformation and fracture (curve c-d). After fracture the contact area of this particle was flattened, suggesting plastic deformation has occurred (as the unloaded particle should be reverted to austenite and the transformation cannot explain this shape change). The fracture occurred by vertical radial cracks as shown in the inset of Figure 3B, which correspond to transverse tensile fracture.

When such single crystal particles are not loaded all the way to fracture, but unloaded after the transformation, they sustain very high stresses at yield (i.e. 3.0 - 4.5 GPa) and allow for very large transformation strains as well. As a result, these particles generally have significantly higher energy dissipation after a complete cycle, reaching $\sim 20 - 40 \text{ MJ/m}^3$; this is higher than that achieved in shape memory alloys such as Ni-Ti, Cu-Al-Mn-Ni and Ni-Ti-Nb alloys ($10 - 20 \text{ MJ/m}^3$) [27,28].

Cyclic loading

Because the single crystal SMC particles exhibit robust superelasticity, we further explored their cycling/fatigue behavior. Figure 5A shows load-displacement curves for particle #5, which has a diameter of $\sim 1.2 \mu\text{m}$. For the first cycle of compression, two clear displacement plateaus (total $\sim 40 \text{ nm}$, $\sim 3.3\%$ compression) associated with stress-induced martensitic transformation are observed in the loading curve, and a displacement plateau of 36 nm upon unloading into austenite phase. A residual displacement of $\sim 13.2 \text{ nm}$ is found after the first cycle, likely due to plastic shape adaptation between the tip, the particle, and the substrate; given the strength of diamond and zirconia, we expect that the quartz substrate is most likely the source of the plastic accommodation. Upon subsequent cycling, the same essential sequence of events is observed repeatedly, but the residual displacement (d_{res}) upon unloading is essentially lost after a few cycles and the system becomes reversible (Figure 5B). The total

displacements induced by martensitic transformation ($d_{a \rightarrow m}$, measured from all the plateaus in the loading curves) fluctuate in a range of ~35-45 nm (~2.9-3.8% compression) over the early shakedown cycles, and then gradually decrease to ~32 nm in the 109th cycle.

Additional subtle changes in the shape of the load-displacement curves resemble the “training” effect well known in shape memory materials in general. For example, initially the forward transformation takes place through a multi-step series of displacement plateau, the bursts approach and then become a single plateau at large cycle numbers. As evidenced in Figure 5C, there is a declining trend in the critical load for inducing martensitic transformation (denoted as $F_{a \rightarrow m}$) and reverse martensitic transformation (denoted as $F_{m \rightarrow a}$) with cycling. Such decrements are generally interpreted as reflecting an evolving competition between different martensite variants, and as substructure develops in the particle it increasingly favors the same kinematic transformation pathway for the same state of loading [29,30]. A similar effect has been reported in fine-grained Ni-Ti and also Cu-Zn-Al shape memory microwires [31] and Cu-Al-Ni micropillars [32]. As a consequence of such training, martensite domains can evolve at lower stresses in the subsequent loading cycles. Once the evolved preferred configuration of martensite domains becomes stable, the cycle shape stops changing as well, and the superelastic cycles (such as the 81st and 109th) become nearly superimposable (Figure 5A). Locally, if we take ten sequential cycles for comparison, the curves are almost exactly reproducible, as shown in Figure 6A-B. These curves thus constitute a kind of superelastic “signature”, similar to that found in many shape memory alloys [33,34].

One more phenomenon associated with the cycling shakedown is the gradual reduction of the area inside the superelastic loop, i.e., the energy dissipated per cycle. A quantitative analysis is presented in Figure 5D, showing a significant reduction from ~30 to ~20 MJ/m³ in the first 20 cycles as the critical load and the total displacement ($d_{a \rightarrow m}$) associated with martensitic transformation ($F_{a \rightarrow m}$) decreased very significantly. From the 20th to the 25th cycle,

the dissipated energy rises due to a shift of the critical load ($F_{m \rightarrow a}$) to lower plateau and also an increment in the total displacement ($d_{a \rightarrow m}$), but afterwards the general decrease continues as the hysteresis loop narrows to its stationary state. This evolution is consistent with the exhaustion of a substructure evolution process, which would be dissipative as long as it were active.

Fatigue

We cycled more than 10 small single crystal particles to failure under uniaxial compression loading, with most of the particles exhibiting a fatigue life of ~50-100 cycles. Particle #5 is examined near the point of failure in Figure 7A. The 109th cycle is relatively typical, and quite like the preceding many dozen cycles that this particle had experienced. However, permanent displacements started to develop from the 110th cycle: beyond the first large displacement burst, a second, failure-related burst was recorded, with a smooth shoulder and large displacement that was not recovered fully on unloading. On the 111th cycle, the particle experienced further permanent distortion. Similar phenomena have also been seen in the other particles (see, for example, Figure 7B). Figure 8 shows a typical particle after experiencing failure as described above. A few cracks can be observed (denoted by arrows) and the particle is in the process of pulverizing.

To better understand the initiation mechanism of the cracks during the fatigue failure of the SMC particles, TEM analysis was carried out on single crystal particle #6 after superelastic cycling 16 times, with the results shown in Figure 9. From the bright field TEM image (Figure 9A), a debris field with what appear to be dislocation lines are observed in the contact area beneath the flat diamond punch and also aligned along the compression direction through the center of the particle (noted by arrows). However, most of the particle volume outside of the cylindrical region defined by the contacts, is essentially clean of dislocations. Figure 9B represents a high resolution TEM image taken from the top contact area and Figure 9C is the corresponding Fast Fourier Transform (FFT). It is consistent with the particle being

in the tetragonal austenite phase (which is reasonable for the present unloaded condition), with a zone axis of $[\bar{2}1\bar{2}]$. Dislocations and stacking faults can be identified. Two Burgers circuits are marked in the regions D-E and indicate edge dislocations.

The debris field seen in Figure 9A is presumably a remnant of the martensitic transformation. No martensite laths are observed, as expected for this particle in which the reverse transformation occurred upon unloading [35] above the Austenite finish temperature. Nevertheless, the dense dislocation lines are supporting evidence that the particle experienced cycles of forward and reverse martensitic transformations, which would indeed be expected to preferentially occupy the central core of the particle where stress lines are concentrated in a compressed particle. What is more, the accumulation of such debris and the associated concentration of stresses between transformed and untransformed regions could lead to the opening of incipient fatigue cracks. To our knowledge, our mechanical tests present the first observation of fatigue in cycled small-volume shape memory ceramics, and it has the appearance of a conventional defect accumulation leading to eventual crack formation. Combined with the observation of significant defect debris in the cycled particle, this suggests that the transformation mismatch even within a single grain can lead to structural degradation that leads to fatigue crack formation. The degree to which this is exacerbated by the strong stress gradients in the Hertzian contact geometry, which would favour partial transformation through the particle, are a subject worthy of greater study.

Conclusion

By using spray drying, micro-scale shape memory ceramic particles of ceria-doped zirconia comprising one grain or a few grains have been produced, and the role of grain structure on the superelastic properties of individual particles tested. Polycrystalline particles failed to exhibit superelasticity, because the stress level to cause intergranular cracking was below that required

to trigger the martensitic transformation; such particles fragmented upon the first mechanical loading. On the other hand, oligocrystal or single crystal particles can exhibit cyclic superelasticity, as they do not fracture before the transformation occurs, giving rise to recoverable transformation strains. Whereas oligocrystal samples still occasionally fracture, and the transformation may in fact exacerbate intergranular fracture, single crystal particles exhibit superelasticity in some cases for more than 100 cycles of loading and unloading. Upon cycling, both the critical load for the forward transformation and the total transformation displacement follow a decreasing trend that is more pronounced in the first 20 cycles due to a “training” effect as the specimen evolves a dislocation substructure. This substructure was observed directly by TEM, and occupies the central cylindrical region of the particle, and after it is fully developed the dissipated energy per superelastic cycle decreases from $\sim 30 \text{ MJ/m}^3$ to $\sim 20 \text{ MJ/m}^3$. These observations represent the first exploration of fatigue structure evolution and failure in small volume shape memory ceramics, and the observation that more than a hundred cycles before fracture are possible in spheroidal particles is encouraging.

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MIT/NTU have jointly applied for a U.S. Provisional Utility Patent (application number: 62/294,402, dated on February 12, 2016) related to the materials and design methods produced in this work. The authors would like to acknowledge Prof. Ali Miserez and Shahrouz Amini for their assistance in using the Hysitron nanoindenter, and Dr. Alan Lai (MIT) for useful discussions.

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