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HYDROGEN/LENGTH SCALE INTERACTIONS DURING SMALL VOLUME YIELDING AND FRACTURE

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ABSTRACT

Nanoindentation and thin-film decohesion experiments in the presence and absence of hydrogen have revealed a connectivity in terms of size scale. We propose this can be qualitatively interpreted in terms of a volume to length scale which is more precisely connected to the local stand-off distance of the nearest dislocation. The latter controls the local stress. This has ramifications to the ductile-brittle transition, thin-film decohesion and threshold stress intensities for hydrogen embrittlement. Interpretation of threshold stress intensity as a function of test temperature in Fe-3wt%Si single crystals as well as thin film decohesion of Cu from silicon after hydrogen charging are discussed.

KEY WORDS

Hydrogen embrittlement, nanoindentation, size scale, dislocation shielding

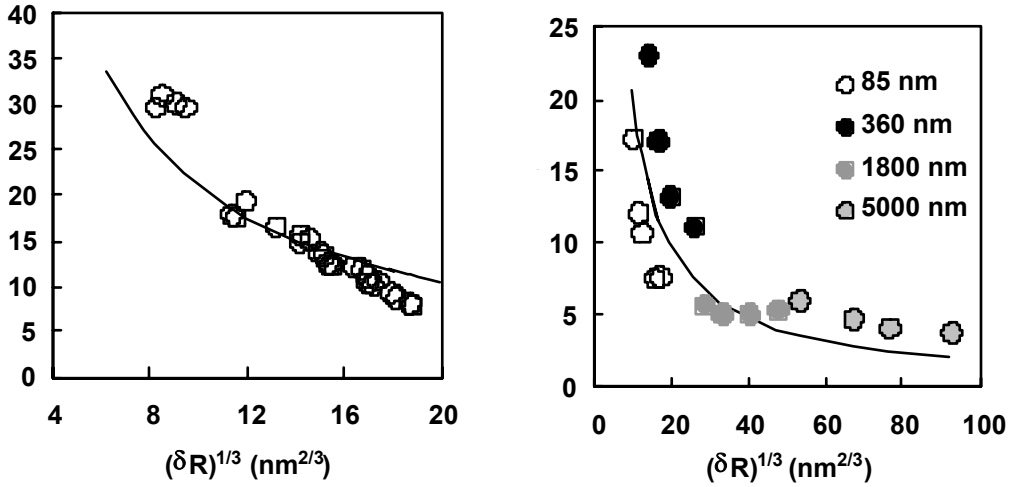
INTRODUCTION

Recent findings on two levels of scale have prompted reexamination of our current understanding of hydrogen embrittlement [1-4]. Specifically, at the nanometer/μN scale, nanoindentation measurements of yield points have exhibited a couple of phenomena. One has led to a size scale plasticity dependence often referred to as the indentation size effect. Here the shallower the penetration depth the harder the material as measured by nanoindentation. Elsewhere in this proceedings this is elaborated upon in length. If the same type of experiment is conducted after electrochemically charging the same sample, small penetration depths give a yield point load that strongly increases with increasing hydrogen content. A second level has involved the micron/μN scale where larger indentations into thin films can produce sufficient stored elastic energy that energy release rates can delaminate the film/substrate interface. In addition, we have electrochemically charged such film/substrates system and have shown the critical strain energy release rates associated with interfacial fracture are reduced by as much as a factor of two [4].

In the present paper we propose a connectivity between these two sets of phenomena and as such an interrelationship between two levels of scale. At best, however, we view this as a work in progress because of the complexity of the phenomena and its interpretation. We will emphasize where progress has been made and point out alternative pathways by which hydrogen "embrittlement" might be understood. The research includes a brief review of the indentation size effect on Fe3%Si and W single crystals and its connectivity to a volume to surface area concept. We then briefly review the modified Rice-Thompson model for the brittle to ductile transition applied to Fe3%Si single crystals in the absence and presence of hydrogen. This is all brought together with a length scale that can be measured independently for thin films of Cu/Ti/SiO_2/Si. Applications to film deadhesion with and without hydrogen utilize the Rice-Thompson approach.

THEORETICAL CONNECTIONS

At the smallest scale discussed here, we have found that extremely large enhancements of hardness exist at depths of penetration in the 10–100 nm range [1,2]. Whereas the hardness, H, might be expected to be about three times the bulk yield stress, σ_{ys}, values of (5–20)σ_{ys} were found for indentation into {100} planes of Fe-3wt%Si and W single crystals. Results [1] and interpretation [2] are given elsewhere, examples being given in Figure 1.



a) b)

Figure 1. Fit of the proposed model [2] for two ⟨100⟩ oriented single crystals. Single tips of 205 nm and 70 nm radii were used in (a) and multiple spherical tips with radii noted were used in (b).

The solid curves in Figures 1(a) and 1(b) represent Eqn. (1) as given by

$$\frac{H}{\sigma_{ys}} = \left\{ \frac{(V/S)^2}{3\delta R} \right\}^{1/3} \tag{1}$$

where V/S is the indent volume to surface ratio, δ is the penetration depth and R is the tip radius of the 90° diamond cones used. For the Fe-3wt%Si this was a 70 nm tip radius while for the W a

variety of tips were used as indicated in Figure 1(b). Tip correction factors were utilized for any penetrations beyond the spherical regime.

In the same study [2] it was noted that *V/S* was constant for the first 100 nm of penetration in a given material. However, it varied from 4.7 to 11.7 μm for four single crystals ranging from tungsten to gold. Since *V/S* is a length scale, this was immediately considered as having a fundamental connectivity to the plasticity process. More details about this are considered in a companion paper as part of this proceedings [5]. We then hypothesized that if this μm-size length scale from nm level experiments represented a microstructural characteristic, might it not be applicable to fracture experiments as well as indentation. While at first glance this might suggest a leap of faith, it is not so strange if you consider the modified Griffith criterion scaling with the relative amount of work associated with crack exposed surface energy and crack-tip plastic volumes. Again, as detailed in the companion paper [5], this analogous behavior for nanoindentation and crack tips is demonstrated. Given that, the step of including hydrogen effects is trivial in concept but complex in detail. That is, hydrogen can be affecting both the surface energy and the plastic work contribution in ways not understood well at all. We [3] and others [6] believe that thin film decohesion, as described in the next section, can provide some of the answers.

In a recent paper and a review, some 25 film/substrate multilayers were evaluated for the effects of film thickness, yield strength, test temperature and interfacial chemistry on delamination toughness [3]. It was concluded that there are brittle to ductile transitions (BDT) in metal films deposited on ceramic or semiconductor substrates. This was analogous to the BDT that occurs when either reducing thickness (increasingly plane stress) or raising test temperature (reducing yield strength) in bulk test specimens. Additional features of this are detailed in the companion paper [5]. One significant feature is that as film thickness decreases, plastic energy dissipation decreases. As shown later under results and discussion, the fracture resistance decreases to the true surface energy of the interface. This allows the local stress intensity ($k_{IG} \equiv \left[2E\gamma_i\right]^{1/2}$) at the Griffith energy level to be established without having to deconvolve the plastic energy dissipation contribution. This may be coupled with a nanometer length scale associated with the distance of the nearest dislocation to the crack tip. Often referred to as a dislocation free zone (DFZ) this leads to the second necessary parameter, *c*. In a series of papers [7], it is shown that if both k_{IG} and *c* are known, use of the Rice-Thomson [8] and Lin-Thomson [9] formalism leads to

$$K_c = \frac{\sigma_{ys} c^{1/2}}{2\exp(4/3)} \exp\left\{\frac{\pi^{3/2} k_{IG}}{6\sqrt{2}\sigma_{ys}(2c)^{1/2}}\right\} \tag{2}$$

Having the yield strength, σ_{ys}, and the Griffith energy which gives k_{IG}, the only unknown is the dislocation stand-off distance, *c*, which controls the local stress and hence the fracture criterion. We believe there is a connectivity between the length scale in nanoindentation, *V/S*, and an approach which should eventually lead to an understanding of the stand-off distance, *c*. While we leave that discussion for the companion paper, a more qualitative argument here is that the number of dislocations in a pile-up follows a similar relationship for cracks and nanoindentations implying the same length scale applies. Approximately six years ago [10] we suggested that observations of crack-tip and nanoindentation-tip emission of dislocations "will eventually lead to more precise mechanisms and solutions for brittle-ductile transition and contact wear phenomena." In a series of papers [7,11,12] we suggested that the number of dislocations in an inverse pile-up might be similar for a yield instability at an indenter or at a crack tip. The number of dislocations in the

respective pile-ups, as calculated elsewhere [5], are shown in Figure 2. This is of some significance and suggests a connectivity of scale over this range as discussed below.

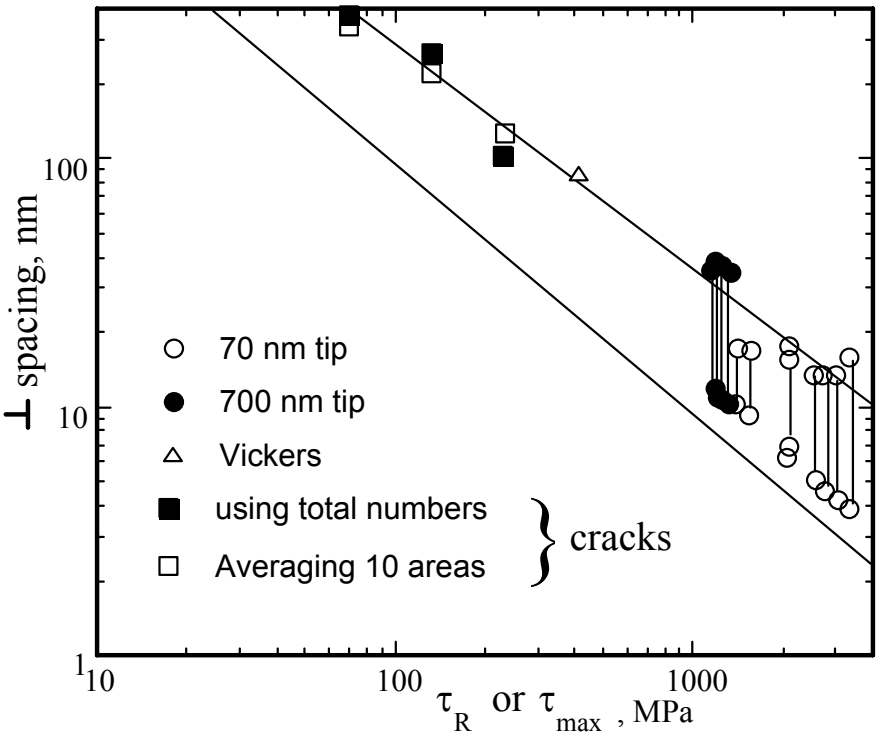


Figure 2. The average dislocation spacing variation with the resolved stress on the slip planes at the crack tips or the maximum shear stress under the indenter. The data range in the 70 and 700 nm tip data are based upon the densest lip band (upper points) and average density of all planes (lower points).

RESULTS AND DISCUSSION

First, we reexamine some hydrogen embrittlement data in Fe-3wt%Si single crystals. We note that this undergoes discontinuous cracking with single forward crack increments of about 0.74 ± 0.12 μm. Such extensions occurred for both externally supplied (1 atm.) or internally supplied (cathodically charged) hydrogen. An example of the latter, not previously published, is shown in Figure 3. Rather than attempting to reexamine kinetics, which is far too complex [14], we will address threshold in the context of the dislocation model presented above.

As discussed elsewhere [5] in this volume, we demonstrate that the lead dislocation for a 22 dislocation pile-up would give a value of 3.2 nm for the "DFZ" which is hardly worth calling a zone. However, Li [15] has recently shown in simulations that additional slip bands emitting can produce a "DFZ" much larger than if a single band is emitting. In fact, a DFZ ranging from 3 to 16 times as large as the distance between the first and second dislocations in front of the DFZ exists. Even though our dislocation arrangements are not identical to the one used [15] we interpreted our 79.5º orientation of slip bands in the context of Li's simulations. From those simulations, it was found that the DFZ could be 15 times as large as our calculated value of 3.2 nm. This would represent a DFZ of 48 nm which is *c* in Eqn. (2). It is important to note that he used 15 emitting slip planes, quantitatively similar to those previously observed. We used this to determine fracture toughness for ‹100›Fe-3wt%Si crystals tested at temperatures from 100 to 298ºK.

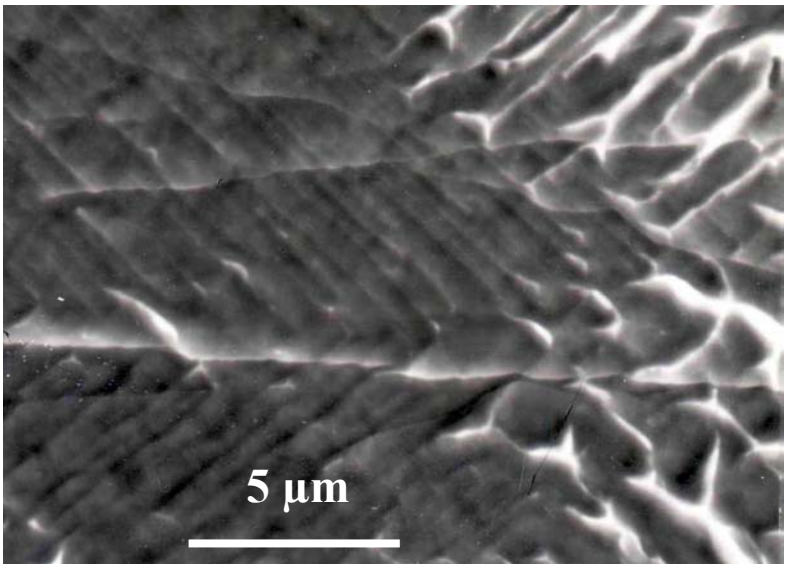


Figure 3. Fracture surface of Fe3%Si indicating discontinuous crack growth during electrolytic hydrogen charging.

The yield strength and average fracture toughness values from the previous study [7] are given in Table 1 for five test temperatures. With a c = 48 nm, the yield strengths observed and a k_{IG} of 0.85 MPa-m$^{1/2}$ as taken from nominal surface energies [7], the agreement is seen to be good between observed and calculated K_{Ic} values.

TABLE 1
Yield strength and fracture toughness, observed and calculated from Eqn. (2) using a value of c = 48 nm.

T, ºK	100	173	233	298	363
σ_{ys}, MPa	450	395	352	305	285
Obs. K_{Ic}, MPa-m$^{1/2}$	6	23	50	120	> 120
Calc. K_{Ic}, MPa-m$^{1/2}$	11.7	22.7	44.6	118	199

Regarding hydrogen effects, the one simple assumption is that the concentration levels involved do not affect the far field yield strength which dictates pile-up behavior. The second one is *ad hoc* and assumes that k_{IG} through the surface energy is reduced to 0.70 MPa-m$^{1/2}$. This is a slightly greater reduction than was found in a previous analysis [5]. This allows an equally good fit to previously published data [17]as seen in Figure 4.

Returning to small volume behavior as represented by thin films, in a review of 14 metal/interlayer/substrate combinations, it was found that the dislocation stand-off distance scaled with $(k_{IG}/\sigma_{ys})^2$. Taking the Griffith value of 0.85 MPa-m$^{1/2}$, for this Fe-3wt%Si single crystal, this correlation shown elsewhere [3] would give a value of $c \sim 500$ nm, an order of magnitude greater than the 48 nm found. This suggests that the longer length of slip bands available in single crystal or coarse grained solids allows greater shielding compared to nanocrystalline thin films. That is, it is well-documented that regular arrays of dislocations can shield the crack tip from the far-field stress. A balance of forces between the stress field of the dislocation array and the stress field of the stress intensity essentially increases the resistance to crack propagation. In the early stages of nanoindentation, this same balance of forces between tip-emitted dislocations and the stress field of the indenter increases the resistance to penetration. In fact, it has been recently shown [5] that

film thickness which partially controls the nanocrystalline grain size is an integral part of the size scale.

In the thin film review it was found that a Cu/Ti/SiO_2/Si film system had a value of c = 60 nm [3].

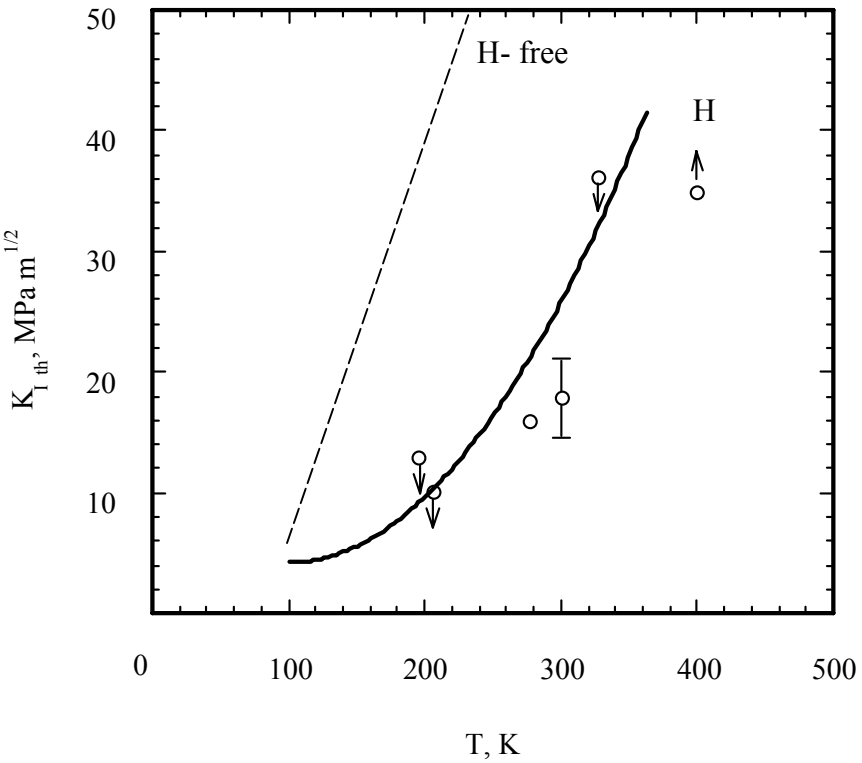


Figure 4. Comparison of Eq. (2) to hydrogen-affected threshold stress intensities for Fe3%Si crystals.

Here, yield strength was given by

$$\sigma_{ys} = \sigma_0\left[1 + \beta h^{-1/2}\right] \tag{3}$$

where σ_0 = 400 MPa, β = 0.287 μm$^{1/2}$ and h = film thickness. With measured values of G_{IG} = 3.6 J/m^2 for interface fracture in Cu/Ti/SiO_2/Si and E = 120 GPa, it was a simple matter to calculate k_{IG} = $(EG_{IG})^{1/2}$ to be 0.66 MPa-m$^{1/2}$ and from that determine c = 60 nm at $K_c = k_{IG}$ using Eqn. (2). The fit to all the data using Eqn. (2) with yield strength varying as a function of thickness from Eqn. (3) is shown in Figure 5. Cathodically charging the same copper films at 60 mA/cm^2 for 70 s in 1 M NaOH reduced the fracture resistance as shown in Figure 5. By allowing a small decrease in the Griffith stress intensity from 0.66 to 0.59 MPa-m$^{1/2}$ due to hydrogen, Eqn. (2) also predicts the decrease in strain energy release rate. For the hydrogen case here, it is seen that a 20% drop in the surface energy can lead to a 50% decrease in the practical work of adhesion for the 1 μm size film in Figure 5.

What does this approach imply for hydrogen embrittlement mechanisms at different levels of scale? Reexamination of Eqn. (2) reveals several aspects perhaps unappreciated prior to recent studies of thin films:

1) At large scale, c can be reasonably small particularly for relatively low yield strength materials such as single crystals or coarse-grain alloys. This can provide large toughness at intermediate temperature in even those materials prone to brittle fracture. At low enough temperatures low energy brittle fracture still prevails in such materials.
2) This does *not* preclude a microscopic fracture mode transition as temperature increases and yield strength decreases. All this implies is that with greater shielding and lower yield strength, $\sigma_{ys}c^{1/2}$ in the denominator of Eqn. (2) decreases with increasing test temperature. This raises K_c exponentially. By elimination of decohesion along either a cleavage plane or an intergranular or bi-material boundary because the necessary K_c is too high (!), the alternative fracture mode is ductile fracture. The same concept applies to hydrogen embrittlement but with additional complexity. Consider stainless steels or superalloys. Does hydrogen reduce k_{IG}, increase σ_{ys} but leave c unaffected? Clearly this does not happen in many stainless steels that fail by microvoid coalescence but perhaps it does in high strength superalloys that fail by intergranular fracture. An intriguing aspect of this is that slip localization would tend to enhance shielding by reducing c. Even if k_{IG} were reduced this could lead to microvoid coalescence as the preferred fracture mode.

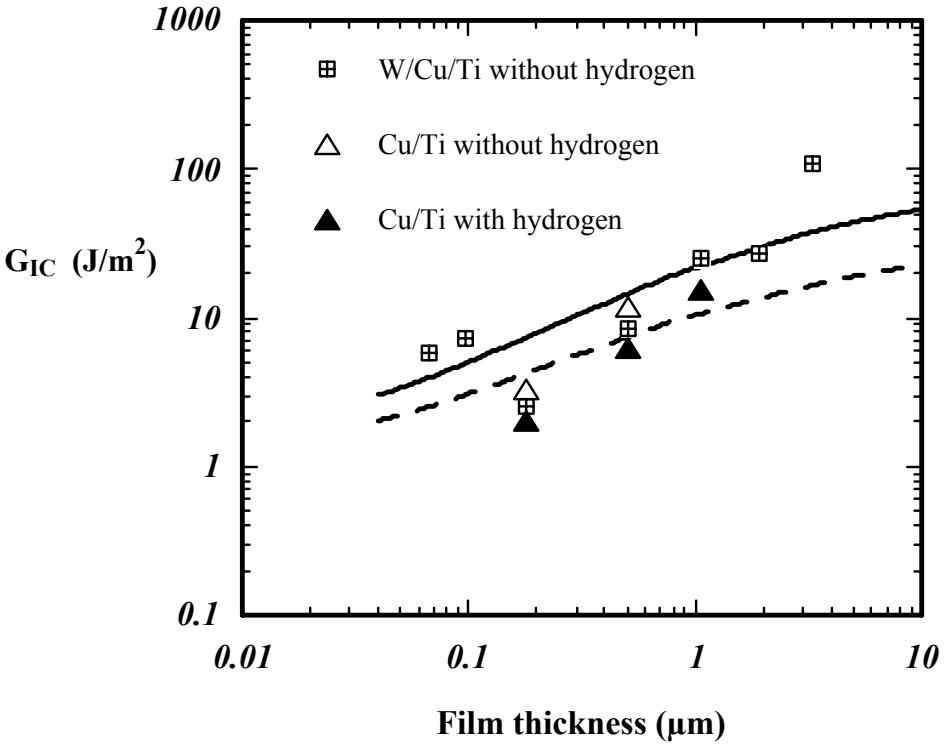


Figure 5. Effect of film thickness on Cu/Ti/SiO2 interfacial fracture resistance with (dashed line) and without hydrogen(solid line).

3) Finally, with respect to small scale, we hypothesize that the values of c can be considerably larger at the same yield strength in thin films compared to larger scale microstructures. The limited shielding available due to restricted lengths of slip bands and numbers of dislocations will tend to give larger values of c and form lower toughness and higher susceptibility to hydrogen embrittlement. This is particularly the case for thin nanocrystalline films with high yield strengths (fine grain size) weakly bonded to a substrate. For such cases it is seen that all three parameters in the exponential, a lower k_{IG} in the numerator and high yield and a larger stand-off distance in the denominator, would favor embrittlement.

SUMMARY

A connectivity of scale in terms of numbers of dislocations emitted at a point source and their average spacing has been established for both nanoindenters and crack tips. Determination of the numbers of parallel slip bands have been indirectly and in some cases directly observed allowing estimates of the number of dislocations per slip band. This gives a crude estimate for the back stress on the source which is surprisingly even much greater for sharp indenter tips than a crack tip. For the same two orders of magnitude displacement scale examined (10–1000 nm), this agreement gives some reason to believe that a consistent length scale is controlling the plastic deformation process. What we have learned with such small scale deformation processes leads to a refined brittle-to-ductile transition model via the Rice-Thomson and Lin-Thomson formalism. This is then easily modified for the hydrogen embrittlement process where either a cleavage plane, a grain boundary or a bi-material thin film interface is degraded. The key here is a length scale dictated by the closest approach of the last dislocation emitted in a shielding array.

ACKNOWLEDGMENTS

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