Development of New Magnetorheological Fluids for Polishing CaF_2 and KDP

Magnetorheological finishing (MRF) is a novel and recently commercialized[1] process for figuring and polishing plano, convex, and concave optics—both spherical and aspherical—from a wide variety of optical materials. A recently written review article provides an overview of the history, theory, and implementation of this technology.[2] The utility and productivity of MRF have been proven for a wide spectrum of optical glasses and demonstrated for a variety of non-glass optical materials.[3,4] A 1.0-nm smoothness with removal rates of 1 to 10 μm/min is routinely achieved. Seven years of research and development culminated in 1998 with QED Technologies' introduction of a commercial MRF machine, designated the Q22. A focus of continuing research is the development of MR fluid compositions and operating parameters to finish optical materials with an ever-widening range of physical properties. Efforts are simultaneously made to extend our understanding of the fundamental mechanisms of material removal in the MRF process. Extremely hard, extremely soft, single-crystal, polycrystalline, or water-soluble optical materials—each presents unique challenges to the MRF process.

A magnetorheological (MR) fluid is a suspension of magnetically soft ferromagnetic particles in a carrier liquid. Typically, the particles are of the order of a few microns in diameter, and their volume concentration is 30% to 40%. When exposed to a magnetic field, the viscosity and yield stress of the suspension increase several orders of magnitude. The transition is rapid and reversible. The magnetically soft media used to manufacture MR fluids, which are subsequently used in MRF, are carbonyl iron (CI) powders. They are prepared by decomposing iron pentacarbonyl,[5] resulting in spherical particles of almost pure iron, typically 2 to 6 μm in diameter. Incorporating nonmagnetic polishing abrasives results in an MR polishing fluid that can be manipulated to form a renewable and compliant sub-aperture lap for optical finishing.

MRF Research Platforms and Polishing Spots

The Center for Optics Manufacturing (COM) has two research platforms to facilitate the continuing research of MRF: The first, commonly known as the horizontal trough machine, was the basis of the first prototype MRF machine (described and shown in Fig. 1 of Ref. 2), which is still routinely used but without the fluid circulation system. The MR fluid resides in a rotating horizontal trough. The test optic must be spherical convex. While technically overshadowed by newer machines, it continues to be very productive. Experiments can be conducted with only about 100 ml of MR fluid. In addition, the machine can be quickly cleaned to prepare for another experiment. This is particularly useful for screening experiments of new nonaqueous compositions.

A new research platform, designated the spot-taking machine (STM), was designed and constructed by QED Technologies and installed at COM in August 1998 (a photograph of this machine is shown in Fig. 80.19). The MR fluid circulation and conditioning system and rotating wheel are identical to that of the commercial MRF machine. The electromagnet and pole pieces are the same as those on the Q22 with one exception: the pole pieces on the Q22 are tapered downward when moving away from the center to create more clearance when polishing concave optics. The conditioner mixes the MR fluid, maintains its temperature, and monitors and controls its viscosity.

The fluid, typically at an apparent viscosity between 0.04 and 0.1 Pa•s (40 to 100 cps, at a shear rate of ~800 s^{-1}), is delivered through a nozzle by a peristaltic pump onto the surface of the vertical rotating wheel moving at approximately 1 m/s. The wheel is a section of a 150-mm-diam sphere. As the MR fluid ribbon is carried into the magnetic field, the fluid viscosity increases approximately three orders of magnitude in a few milliseconds and becomes a Bingham plastic fluid.[1,2] The high gradient of the magnetic field has the effect of segregating a portion of the nonmagnetic polishing abrasive to the upper layer of the polishing ribbon.[1,6] The surface of the optic is inserted typically 0.5 mm into the ribbon at this point on the wheel, forming a continuously renewed compliant sub-aperture lap. After flowing under the optic, the wheel carries the fluid out of the magnetic field, where it returns to its original low-viscosity state. A collection device removes the

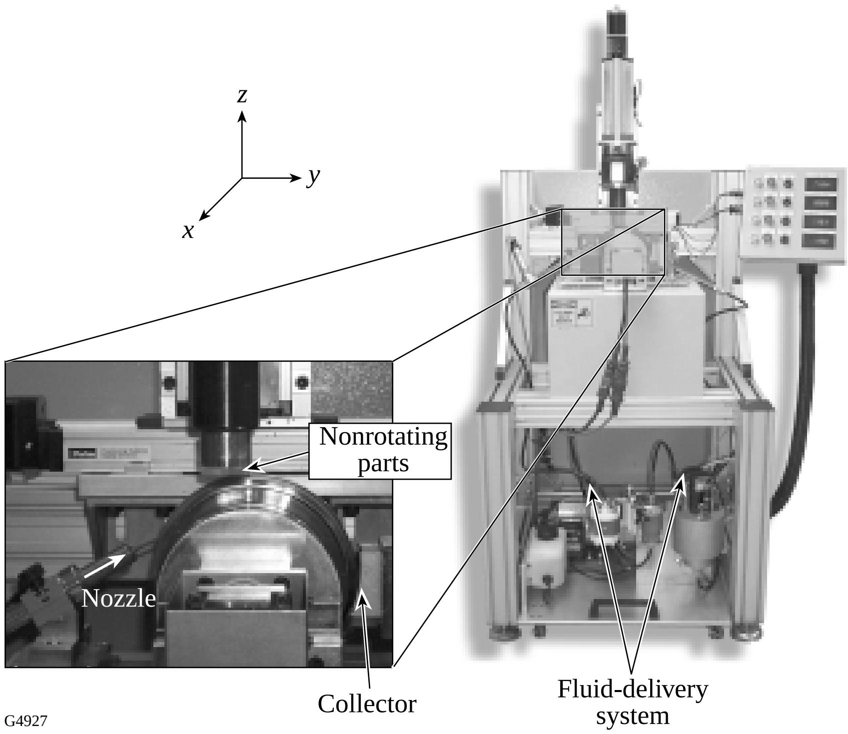

Figure 80.19
A new MRF research platform, the spot-taking machine, incorporates the same fluid-delivery system and vertical wheel as the commercial MRF machine.

fluid from the wheel and returns it to the conditioning system. A typical charge for the system is 1 liter of fluid, which lasts for two weeks of operation.

The STM has a single *z*-axis controller (see Fig. 80.19) to position a test flat into the ribbon for a programmed length of time, typically just a few seconds, and then remove it. The *y*-axis position (parallel to the ribbon) and spindle rotation can be manually adjusted to put multiple spots on a given test flat. The small volume removed, measured interferometrically, is called a "spot" or removal function. Figure 80.20 shows examples of interferograms of spots on two test flats.

By analyzing spots made with these two research platforms we can make critical evaluations on candidate MR fluid compositions. The dimensions of the spots can be measured interferometrically[7] to calculate material-removal rates and measure spot profiles. The surface texture within the spot can be optically profiled[8] to quantify microroughness and reveal surface defects. This information is then used to make informed decisions regarding changes to the fluid composition and/or machine parameters. In addition, the fluid is observed to see that it can be successfully pumped through the delivery system and that it forms a stable ribbon.

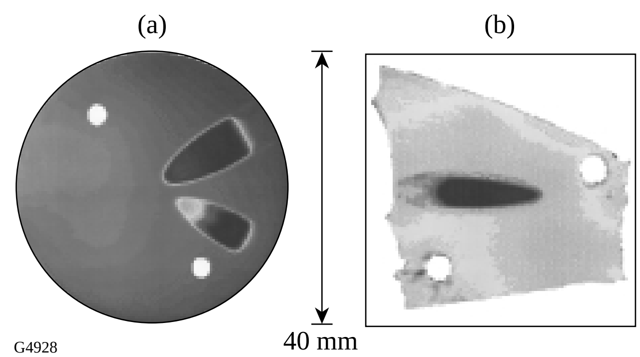

Figure 80.20
(a) An example of an interferogram of two spots made on a CaF_2 test flat. (b) An interferogram of a spot made on a shard broken from a larger plate of KDP. Fiducial marks are used to align interferograms of the original and spotted test flat. Subtraction of the original from the spot interferogram gives the removal function.

One advantage of MRF is the range of operating parameters that can be manipulated to influence the characteristics of the removal function. These include

- MR fluid composition: Carbonyl iron type and concentration, nonmagnetic abrasive type and concentration, carrier fluid and stabilizers can all be adjusted. For aqueous compositions, the MR fluid viscosity can be changed in real-time by adding or removing water.

- Magnetic field: Increasing the magnetic field increases both the stiffness of the ribbon and the removal rates. The practical upper limit is near the saturation magnetization of the magnetic particles. The practical lower limit is where the ribbon is not held tightly against the wheel, resulting in uneven flow under the optic.

- Wheel speed: The removal rate is proportional to the wheel speed. A typical value is 150 rpm but it can be varied from 100 to 400 rpm (0.79 to 3.15 m/s, 150-mm-diam wheel).

- Nozzle: Nozzles with different diameter and shaped orifices can be installed. The standard nozzle is circular and 3 mm in diameter.

- Ribbon height: Increasing the flow rate, typically between 0.5 and 1.0 liter/min, increases the height, or thickness, of the ribbon for a given wheel speed. A typical height is 1.0 to 2.0 mm.

- Depth (inversely, gap): Decreasing the gap between the optic and the wheel increases the depth of penetration into the ribbon and increases the area, or footprint, of the spot.

This range of operating conditions permits many options when conducting experiments on a wide variety of optical materials.

MRF of CaF_2 and KDP

In this article we present details of recent work to adapt MRF to two soft, single-crystal optical materials: calcium fluoride, CaF_2, and potassium dihydrogen phosphate, KH_2PO_4 or KDP. It was necessary to formulate two new magnetorheological fluid compositions in order to successfully apply MRF to these two materials. The standard MR fluid, suitable for a wide variety of optical materials, consists of (in vol %) 36% CI, 55% water, 6% cerium oxide, and 3% stabilizers. CaF_2 is incompatible with the standard MR fluid typically used for optical glasses, resulting in "sleeks" and unacceptable roughness. KDP is extremely water soluble and therefore also cannot be finished with the standard aqueous MR fluid. Some mechanical properties for these two materials are compared to typical optical glasses in Table 80.II.

Results with CaF_2

Single-crystal calcium fluoride is the optical material that is expected to meet the projection and illumination requirements for photolithography optics as the semiconductor industry begins the transition from 365 and 248 nm to 193 and 157 nm.[15] CaF_2 crystals are fairly soft, so the polishing technique used must carefully reduce surface roughness without creating surface sleeks or fine scratches. These defects can lead to scattering, subsurface damage, and microscopic flaws in a coated surface.[16] In addition, CaF_2 is thermally sensitive, anisotropic, and easily chipped. Manufacturing large optics, such as 100-mm catadioptic cubes or 400-mm refractive lenses, by conventional means is nontrivial.[17,18] A $\lambda/10$ flatness specification at 193 nm is more than three times tighter than a $\lambda/10$ specification at 633 nm.[18] Fortunately, as discussed elsewhere,[2] one of the greatest strengths of MRF is its ability to deterministically finish optics to very high precision.

Table 80.II: Physical properties of CaF_2 and KDP compared to typical optical glasses.

Material	Source	Structure	Water solubility (g/100 g)	Near-surface hardness (GPa)	Young's modulus (GPA)	Fracture toughness (MPa-m$^{0.5}$)
KDP	Cleveland Crystals, Inc.	single-crystal tetragonal, type-II cut	33 (Ref. 10)	2.16 (Ref. 14)	49.2 (Ref. 14)	0.1-0.2 (Ref. 13)
CaF_2	Optovac, Inc.	single-crystal cubic c-cut	0.0017 (Ref. 9)	2.47 (Ref. 14)	110 (Ref. 12)	0.33 (Ref. 12)
BK-7	Schott, Ohara	glass	insoluble	7.70 (Ref.14)	79.6 (Ref. 14)	0.85 (Ref. 11)
Fused silica	Corning	glass	insoluble	9.79 (Ref. 14)	74.7 (Ref. 14)	0.75 (Ref. 11)

The initial strategy for developing an MR fluid for polishing CaF_2 called for the replacement of cerium oxide as the nonmagnetic abrasive and making the fluid more gentle due to the softness of this material. Toward this end, many fluid compositions were screened with spot experiments using the horizontal trough machine. For all of the experiments with CaF_2, the test optics were initially pitch polished to an average rms roughness of 0.85±0.05 nm. Compositions containing (in vol %) 36% CI, 25% PEG 200, 38% water, <1% stabilizers, and then a fraction of a percent of nanodiamond powder[19] were tested to determine material-removal rates and microroughness. PEG 200[20] was included because of its lubricious behavior, which was intended to protect the surface from scratching and eliminate embedded particles. Figure 80.21 is a plot of the peak removal rate for a range of nanodiamond concentrations. The removal rate rises quickly with nanodiamond concentration but rolls over above ~0.1 vol %. The roughness values within the generated spots varied from 1.0 to 1.65 nm and showed no clear trend as a function of nanodiamond concentration.

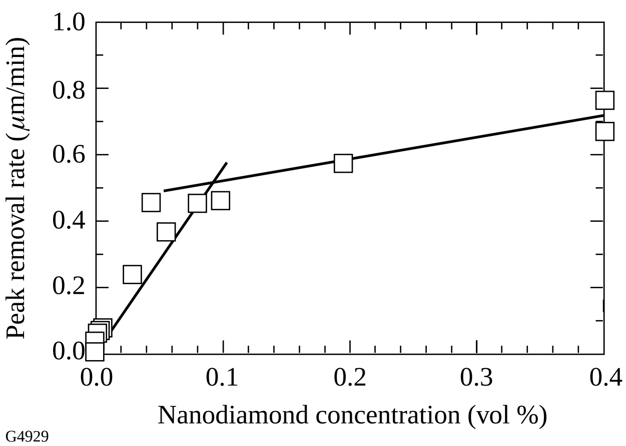

Figure 80.21
Plot of peak removal rate for CaF_2 versus nanodiamond concentration on the trough machine for MR fluid containing 36% CI, 25% PEG 200, 38% water, and <1% stabilizers.

Although it is possible to magnetorheologically finish CaF_2 to low roughness values with compositions containing PEG 200 and nanodiamonds, the very low peak removal rates observed encouraged us to revisit water-based compositions. For this reason, we tested a MR fluid containing (in vol %) 48% CI, 49% water, 3% stabilizers, and ~0.2% nanodiamond powder. This slurry composition had been developed and previously tested for MRF of very hard materials, such as SiC and sapphire, and was found to be rheologically stable. Spots made on the horizontal trough machine at a 3.0-kG magnetic field strength resulted in a very stiff ribbon and very high peak removal rates > 8 μm/min; however, the rms roughness values were consistently ~2.0 nm. Decreasing the magnetic field strength to 0.85 kG decreased the peak removal rate to 1.3 μm/min but also decreased the rms roughness to ~1.25 nm. This indicated that decreasing the magnetic field strength and decreasing the stiffness of the fluid ribbon would produce lower values of surface roughness.

The same composition was next tested in the STM. Spots were made at three levels of magnetic field strength. At a value of 0.34 kG, it was discovered that the ribbon was very soft and formed a large, ill-defined spot. The peak removal rate was an acceptable 1.6 μm/min, but the spot shape was not usable. Increasing the magnetic field strength to 0.98 kG produced a stiffer ribbon and well-defined spot. The resulting peak removal rate was very high, 7.8 μm/min, and the average rms roughness was very good at 1.00±0.06 nm. At 1.85 kG the peak removal rate increased even further to 11.8 μm/min, and the rms roughness was slightly higher at 1.15±0.06 nm. (These results are summarized in Table 80.III.) Extended life testing in the STM and the Q22 confirmed the composition to be sufficiently stable over time for polishing trials.

Table 80.III: Peak removal rate and roughness for MRF spots on CaF_2 at various magnetic field strengths.

Magnetic field (kG)	Peak removal rate (μm/min)	Microroughness
0.34	1.6	poor spot shape
0.98	7.8	1.00±0.06
1.85	11.8	1.15±0.06

Results with KDP

KH_2PO_4, or KDP, is an important electro-optic material. It is currently used for frequency conversion of LLE's OMEGA laser. It will be part of the National Ignition Facility's laser under construction at Lawrence Livermore National Laboratory. It is also commonly used in electro-optic devices such as Pockels cells.[10]

Polishing KDP poses several difficult challenges: KDP is expensive in large sizes. It is difficult to polish high-aspect-ratio KDP flats with conventional pitch-lapping techniques. KDP is extremely soluble in water. To magnetorheologically finish KDP, the MR fluid carrier liquid must be nonaqueous, and it must be possible to clean the MR fluid off of the optic with a KDP-compatible solvent. Finally, KDP is very soft with a near-surface hardness of 2.16 GPa (Berkovich microindentor, 5-nN load).

Currently, single-point diamond turning (SPDT) is considered state of the art for finishing KDP, yielding surfaces with 1.0- to 3.0-nm rms roughness.[21] This process is capable of producing 30-cm-diam flat plates for use in large laser systems. SPDT is done by showering mineral oil over the workpiece. This provides lubricity for cutting and helps to control temperature. The oil is removed from the KDP surface with toluene or xylene.

Many oil-based MR fluid compositions have been developed for use in mechanical engineering applications.[6] For practical reasons, it is highly desirable to use a carrier fluid that is nonflammable and capable of being cleaned out of a MRF machine with aqueous-based detergents. During the search for an MR fluid for KDP, chemical compatibility issues became a serious concern. A number of tested water-miscible fluids were found to leave a “fog” on the surface of KDP. (Results of compatibility tests are summarized in Table 80.IV.) Even just a few minutes of contact with 200-proof ethanol transfers enough moisture from the air to leave visible defects on the surface of a KDP flat. Several otherwise-promising MR fluid compositions had to be discarded for this reason. After numerous trials, the base composition found to produce the best results with KDP consisted of (in vol %) 40% CI and 60% dicarboxylic acid ester. This carrier liquid has a very low vapor pressure, does not evaporate, and is easily cleaned out of the STM. This nonaqueous MR fluid is shear-thinning with a viscosity of 0.09 Pa•s (90 cps) at a shear rate of 800 s^{-1} (approximately the shear rate for the fluid in the delivery nozzle of the STM).

The results reported in this article were obtained on surfaces of KDP that were initially prepared by single-point diamond turning.[22] The average rms roughness of this initial surface (five measurements over five sites[8]) was 1.5±0.2 nm. A representative optical roughness map of the initial diamond-turned surface is shown in Fig. 80.22. The turning marks are clearly visible.

Spots were first made with the MR fluid without any nonmagnetic abrasive under a fixed set of conditions.[23] An example of profile scans of a spot[7] are shown in Fig. 80.23. The peak removal rate, calculated from a depth of deepest penetration of the spot, 0.53 μm, was 1.59 μm/min. The rms microroughness was increased to 6.4±0.8 nm. Figure 80.24 gives an optical roughness map of the surface within this spot. The grooves from the flow of the MR fluid are clearly visible.

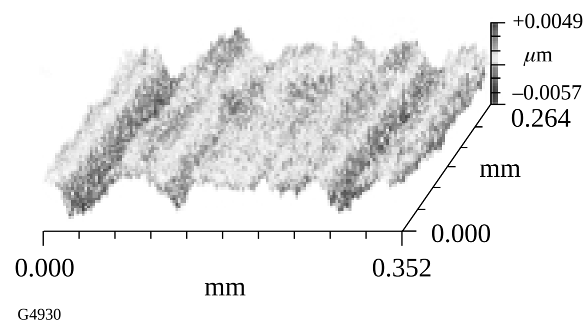

Figure 80.22
Representative optical roughness map[8] of the initial single-point-diamond-turned surface of KDP used for these experiments. The diamond-turning marks are clearly visible. Microroughness: pv = 15.6±3.9 nm; rms = 1.5±0.1 nm.

Table 80.IV: KDP compatibility test results for candidate carrier fluids.

Fluid	Results/Comments
Glycerol	No fogging; viscosity too high for pumping in STM
Ethylene glycol	Serious fogging in just a few seconds of contact
Polyethylene glycol, M.W. 200	Light fogging after several minutes; halo around MRF spots
Liquid paraffin	No fogging in 60 min; oil-based carrier fluid undersirable
Decahydronaphthalene	No fogging; too volatile
Ethanol, 200 proof	Fogging when exposed in air; not in dry N_2; too volatile
Dicarboxylic acid ester	No fogging after extended contact; no halo around spots

The original diamond-turning marks, which would be running approximately perpendicular to the MRF grooves, have been eliminated. The removal rate was in a convenient range, but the goal was not to increase the surface roughness.

Nanodiamond powder[19] was then added to the MR fluid, corresponding to a nominal concentration of 0.05 vol %. The addition of this amount of abrasive had no effect on the MR fluid viscosity. Spots taken with this fluid under the same conditions[23] showed that the peak removal rate increased moderately to 2.10 μm/min. But more importantly, the rms microroughness of 1.6±0.2 was essentially unchanged from that of the initial diamond-turned surface. Figure 80.25 gives a representative optical roughness map of the surface within this spot. The addition of nanodiamonds also decreased the amplitude of the grooves formed by MRF. We expect that these grooves would be eliminated entirely with part rotation during full-scale polishing runs.

The KDP surfaces produced by MRF have been evaluated for laser-damage resistance at LLE. Results are summarized in Table 80.V. MRF maintains the high laser-damage threshold of a diamond-turned KDP part at both λ = 351 nm and λ = 1054 nm.

In light of these encouraging results on KDP with this new slurry composition, the next scheduled task is to scale up to full polish runs on a production MRF machine like the Q22. This will allow a quantitative evaluation of removal efficiency, figure correction capability, and smoothing.

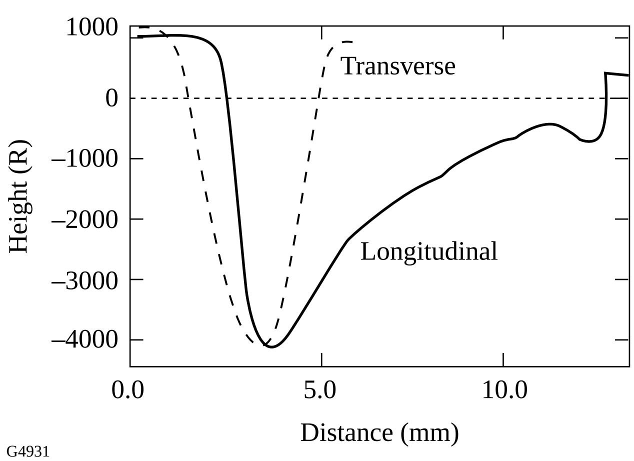

Figure 80.23
Longitudinal and transverse profile scan[7] of a spot made on SPDT KDP with MR fluid without nonmagnetic abrasive. Peak removal rate was 1.59 μm/min; depth of deepest penetration was 0.53 μm.

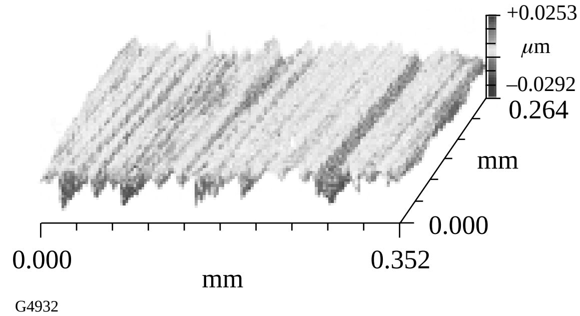

Figure 80.24
Optical roughness map[8] of spot made on SPDT KDP part using MR fluid without nonmagnetic abrasive. Microroughness: pv = 64.8±15.8 nm; rms = 6.4±0.8 nm.

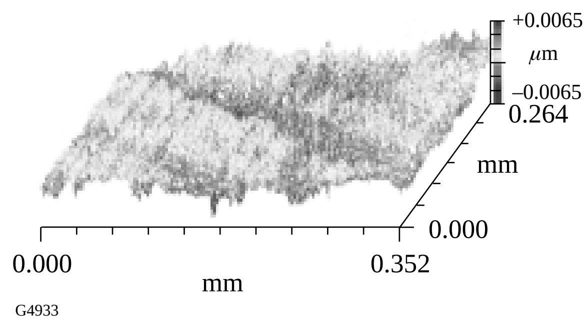

Figure 80.25
Optical roughness map[8] of surface within spot made on SPDT KDP part with MR fluid with 0.05-vol % nanodiamond abrasive. Microroughness: pv = 20.1±7.1 nm; rms = 1.6±0.3 nm.

Summary

This article shows how sub-aperture removal functions, i.e., polishing "spots," are generated on test flats using two magnetorheological finishing (MRF) research platforms. Evaluation of polishing spots is used to further our understanding of MRF and to extend its capabilities to new classes of optical materials. Examples are presented that demonstrate how new MR fluid compositions and operating parameters may be developed for processing CaF_2 and KDP using the evaluation of polishing spots.

ACKNOWLEDGMENT

Support for this work is provided by the Center for Optics Manufacturing, QED Technologies LLC., the U.S. Army Materiel Command, and DARPA.

Table 80.V: Laser-damage test results for KDP parts processed with MRF and SPDT.

J/cm^2	@ 3ω, 1 ns		@1ω, 1 ns	
	1-on-1	N-on-1	1-on-1	N-on-1
MRF	11.23±0.61	14.08±1.06	12.17±1.80	14.76±1.67
Diamond turned	10.63±0.68	14.56±1.08		

REFERENCES

1. D. Golini, Laser Focus World **34**, 187 (1998).
2. D. Golini *et al.*, "Magnetorheological Finishing (MRF) in Commercial Precision Optics Manufacturing," to be published in *Optical Manufacturing and Testing III*, edited by H. P. Stahl (SPIE, Bellingham, WA, 1999), Vol. 3782.
3. D. Golini, S. Jacobs, W. Kordonski, and P. Dumas, in *Advanced Materials for Optics and Precision Structures*, edited by M. A. Ealey, R. A. Paquin, and T. B. Parsonage, Critical Reviews of Optical Science and Technology (SPIE, Bellingham, WA, 1997), Vol. CR67, pp. 251–274.
4. S. D. Jacobs, F. Yang, E. M. Fess, J. B. Feingold, B. E. Gillman, W. I. Kordonski, H. Edwards, and D. Golini, in *Optical Manufacturing and Testing II*, edited by H. P. Stahl (SPIE, Bellingham, WA, 1997), Vol. 3134, pp. 258–269.
5. F. L. Ebenhoech, Prog. Powder Metall. **42**, 133 (1986).
6. B. Berkovski, ed. *Magnetic Fluids and Applications Handbook*, UNESCO Series of Learning Materials (Begell House, New York, 1996), Chap. 6.
7. Zygo Mark IVxp™ or Zygo GPIxpHR™ phase-shifting interferometer systems were used for all data acquisition and analysis related to polishing spots, workpiece surface figure, and transmitted wavefront quality reported in this paper; Zygo Corporation, Middlefield, CT 06455.
8. Zygo NewView™ 100 White Light Optical Profiler, areal over 0.25 mm × 0.35 mm with a 20× Mirau objective, no filter; Zygo Corporation, Middlefield, CT 06455.
9. R. C. Weast, ed. *CRC Handbook of Chemistry and Physics*, 68th ed. (CRC Press, Boca Raton, FL, 1987).
10. J. T. Milek and M. Neuberger, *Linear Electrooptic Modular Materials*, Handbook of Electronic Materials, Vol. 8 (IFI/Plenum, New York, 1972).
11. J. C. Lambropoulos, S. Xu, and T. Fang, Appl. Opt. **36**, 1501 (1997).
12. W. F. Krupke *et al.*, J. Opt. Soc. Am. B **3**, 102 (1986).
13. Value varies with orientation. T. Fang, "Near-Surface Mechanical Properties of Optical Materials in Deterministic Microgrinding," Ph.D. thesis, University of Rochester, 1997.
14. Nano IIs nanoindentor, 5-mN load, Nano Instruments, Oak Ridge, TN 37830; Berkovich indentor.
15. R. DeJule, Semicond. Int. **22** (1), 36 (1999).
16. R. DeJule, Semicond. Int. **22** (2), 38 (1999).
17. R. DeJule, Semicond. Int. **22** (3), 36 (1999).
18. D. Collier and W. Pantley, Laser Focus World **34**, 63 (1998).
19. Dianan® Nano Diamond powder, Straus Chemical Corporation, Elk Grove Village, IL 60007.
20. Carbowax® Polyethylene Glycol 200, Union Carbide Corporation, Danbury, CT 06817-0001.
21. R. C. Montesanti and S. L. Thompson, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-ID-121651 (1995).
22. Cleveland Crystals Inc., Cleveland, OH 44110.
23. Experimental parameters: wheel speed, 150 rpm; magnet current, 15.0 amps (2.22 kG); ribbon height, 2.0 mm; depth into ribbon, 0.5 mm.