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14. ABSTRACT

Tribometric measurements on as-deposited sputtered AlCuFe films are performed using an oscillating pin-on-flat tribometer located within a high vacuum chamber. The coefficient of friction (COF) is measured as a function of temperature between room temperature and 200°C in vacuum as the flat oscillates relative to the pin at an average sliding speed of 3-4 mm/sec. The COF for all AlCuFe films studied was about 0.5 at room temperature and about 0.25 at 200°C. The reflectance of as deposited and annealed AlCuFe films has been measured across a wavelength range from 0.28 to 26.0 microns. The as-deposited reflectance increases from 0.6 at 1 micron to 0.85 at 20 microns, whereas the reflectance of the annealed film is about 0.6 across the entire wavelength range. The resistivity of an as-deposited film, as measured with a 4-point probe, is about 0.4 milliohm cm, whereas after it is annealed into the icosahedral phase, the resistivity increases almost a factor of four to 1.5 milliohm cm.

15. SUBJECT TERMS
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TRIBOMETRIC, OPTICAL, AND ELECTRICAL PROPERTIES OF SPUTTERED QUASICRYSTALLINE ALLOYS

Final Report for the period 01 January 2002 to 31 December 2002
AFOSR Contract Number F49620-01-C-0019

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Submitted by:
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1.0 EXECUTIVE SUMMARY

Ten micron thick AlCuFe films have been sputtered by Technology Assessment and Transfer that can be annealed to yield quasicrystalline (icosahedral) structure. If the sputtering parameters are slightly varied, the sputtered films yield crystalline structure after annealing. We report on a set of experiments which compare physical properties of films which yield icosahedral structure after annealing to those that don't.

Tribometric measurements are performed using an oscillating pin-on-flat tribometer located within a high vacuum chamber. The coefficient of friction (COF) is measured as a function of temperature between room temperature and 200°C in vacuum as the flat oscillates relative to the pin at an average sliding speed of 3-4 mm/sec. The COF for all AlCuFe films studied was ~0.5 at room temperature and ~0.25 at 200°C. However, differences in the transition to a lower friction state between different AlCuFe sputtering runs have been observed.

The reflectance of as deposited and annealed AlCuFe films has been measured across a wavelength range from 0.28 to 26.0 microns. The as-deposited reflectance increases from 0.6 at one micron to 0.85 at twenty microns, whereas the reflectance of the annealed film is ~0.6 across the entire wavelength range.

Finally, we report on measurements of the electrical DC resistivity of as-deposited and annealed AlCuFe films on alumina which were performed using a 4-point resistivity probe. The resistivity of an as-deposited film is $\sim 0.4 \times 10^{-3}$ Ohm cm, whereas after it is annealed into the icosahedral phase, the resistivity increases almost a factor of four to 1.5×10^{-3} Ohm cm.

2.0 INTRODUCTION

We have provided a range of measurements on the properties of sputtered AlCuFe films to aid in the development of a fundamental understanding between sputtering parameters, film composition, microstructure, and properties such as surface energy, friction coefficient, hardness, wear, reflectance, and electrical resistivity. Other team members are AFRL/MLBT, University of

Michigan, Northwestern University, and Carnegie-Mellon University. The films are prepared by magnetron sputtering and characterized by XRD by Technology Assessment & Transfer.

3.0 EXPERIMENTAL

3.1 General Tribometric Test Procedures And Specimens

Friction measurements are performed using an oscillating pin-on-flat tribometer located within a high vacuum chamber (P< 5E-6 Torr) which is shown in Figure 1. The coefficient of friction (COF) is measured as a function of temperature between room temperature and 200°C in vacuum as the flat oscillates relative to the pin at an average sliding speed of 3-4 mm/sec under a normal load of 15g as shown in Figure 2 and Figure 3. The flat oscillates at about 0.5 Hz and the length of the wear track is about 3mm. The temperature is measured by a thermocouple that is embedded in the zirconia support structure and is located just below the Pt heater. A more detailed description of the apparatus and test procedure can be found in reference [1].

We have performed tribometric measurements on two different pin/flat sets, one from AlCuFe sputtering run #1058 and the other from AlCuFe sputtering run #1075. In each case, both the alumina pin and flat is coated by magnetron sputtering with film that is 8-10 microns thick by TA&T. The coatings from run 1058 have a crystalline cubic structure after annealing as opposed to the coatings from run 1075 which exhibit quasicrystalline icosahedral structure after annealing at 500C in vacuum for 2.5 hrs. The coated pin/flat sets have <u>not</u> been annealed prior to our tribometric measurements.

3.2 Friction and Wear of AlCuFe Sputtered Coatings in Vacuum

The coefficient of friction (COF) as a function of cycle number for the 1058 and 1075 pin/flat sets is shown in Figure 4 and Figure 5. During the experiment the temperature is ramped up to 600C at 35 C/min and then back down to room temperature at 35 C/min. The COF is continuously measured throughout the heating and cooling cycles.

The COF for both the 1058 and 1075 samples shows the same qualitative behavior with the COF being around 0.5 – 0.7 at room temperature and around 0.2 – 0.3 at 600C. There is a transition from the higher friction state to the lower friction state that occurs at an intermediate temperature between room temperature and 600C. As the temperature is reduced the COF undergoes a transition back to the high friction state. This behavior is repeatable over multiple experiments in the same wear track as well as experiments in different wear tracks. The fact that the friction transition is reversible suggests that either the transformation of the 1075 coatings to the quasicrystalline state isn't occurring during the heating cycle or that the friction behavior is independent of the crystal structure of the coating. In order to shed light on this, we conducted an experiment where the temperature is ramped up at the typical 35C/min rate and then the pin/flat oscillation is stopped and the temperature is held constant at 600C for about two hours, then the pin/flat oscillation is restarted and shortly after that the temperature is reduced back to room temperature at 35C/min. The two hour exposure to 600C should enable the conversion to the quasicrystalline structure. The results of this experiment are shown in Figure 6 indicating that even with this long exposure to 600C, the COF still increases back to its room temperature value upon cooling. This would seem to suggest that the friction behaviors of the cubic and icosahedral structures of AlCuFe are very similar. Another possibility is that the temperature of the AlCuFe coating isn't as high as the temperature indicated by the thermocouple below the heater in which case the annealing process wouldn't have occurred or it would have taken much longer than two hours.

Before we turned to the issue of the temperature difference between the AlCuFe coating and the thermocouple below the heater, we decided to see if there was any change in the friction behavior with a change in temperature ramp rate for the 1075 pin/flat set. The pin is moved over to a new track (Track 3) and an experiment is performed with a 20C/min ramp rate (Figure 7) and then another experiment is performed in the same track at 25C/min (Figure 8). The COF as a function of thermocouple temperature is shown for 35C/min, 25C/min, and 20C/min ramp rates in Figure 9. There is little difference between the three curves and so the ramp rate, across this range, doesn't appear to affect the tribometric behavior. Evidently a 35C/min ramp rate isn't so fast that the temperature of the coating lags behind the temperature of the thermocouple on the warming ramp.

In order to determine the temperature difference between the thermocouple below the heater and the top surface of the AlCuFe coating on the tribo flat, we performed an experiment in which another thermocouple was squeezed between the pin and the flat to directly measure the pin/flat interface temperature. There was no sliding motion of the flat relative to the pin in this experiment. The heater power is ramped up so that the temperature of the thermocouple below the heater increases at a steady rate of 25C/min and the pin/flat temperature is recorded as a function of the temperature of the thermocouple below the heater. As shown in Figure 10, the pin/flat interface temperature only gets up to 200C even when the thermocouple below the heater is at its maximum temperature of 750C. This data for the warming and cooling ramps can be used to plot the COF as a function of the pin/flat interface temperature (Figure 11). This suggests that the temperature of the transition to the lower friction state occurs around 100-150 C and that the surface of the AlCuFe coating only gets to a maximum temperature of about 225C. Evidently the low thermal conductivity of the alumina tribo flat and the AlCuFe coating reduce heat transport to the pin/flat interface. It seems unlikely then that the 1075 AlCuFe coating has been annealed into the quasicrystalline state. The reduction in COF at an elevated temperature seems to be a feature of as-deposited AlCuFe coatings generated using the 1058 and 1075 sputtering parameters and target stoichiometry.

Figure 12 and Figure 13 show SEM images of the 1058 and 1075 pin/flat sets prior to tribometric measurements. Figure 14 and Figure 15 show SEM images of the 1075 and 1058 pin tips after a number of tests. The wear rate can be estimated by the size of the wear scar on the pin tips and for both the 1075 and 1058 samples, the wear rate is estimated to be 7E-12 $m^3N^{-1}m^{-1}$. Figure 16 shows composition results from EDX of the pin/flat sets.

3.3 Reflectance of As-Deposited and Annealed AlCuFe Sputtered Coatings

The reflectance of AlCuFe coatings on alumina and steel both in the as-deposited and annealed states has been measured using two different instruments. A Perkin-Elmer Lambda 9 dual beam spectrophotometer with integrating sphere attachment is used to measure the reflectance from 0.28 – 2.5 microns. A Gier-Dunkle heated cavity IR Reflectometer is used to measure the reflectance from 5 – 26 microns. Results for samples from coating runs 1060, 1061, and 1079 are shown in Figure 17 and Figure 18. For all samples, the as-deposited reflectance is fairly constant from 0.3 – 1.0 microns, but then increases with wavelength reaching a value of 0.8 – 0.9 at 26 microns. In contrast, the annealed samples have a relatively constant reflectance across the 0.3 – 26 micron range of about 0.5 – 0.6. This is consistent with results obtained by other authors [2].

3.4 Electrical Resistivity of AlCuFe Sputtered Coatings

Several measurements of the electrical resistivity of the AlCuFe coatings were performed using a 4-point probe. The electrical resistivity of quasicrystalline AlCuFe is considerably higher than the electrical resistivity of crystalline AlCuFe and therefore is a good indicator of the transition to the quasicrystalline state. Typical measurements of electrical resistivity by other authors have yielded results in the range 2-3 mΩ cm [3]. Figure 19 shows the electrical resistivity of as-deposited and annealed AlCuFe coatings from sputtering runs 1060 and 1061. The electrical resistivity increases by almost a factor of 10 to around 2.5 mΩ cm after the annealing process which was performed at Raytheon. The annealing was done in high vacuum (10^{-6} Torr range) and consisted of three steps: 1) two hour ramp to 500C, 2) 2.5 hour dwell at 500C, 3) two hour ramp down to room temperature. The increase in electrical resistivity and the actual resistivity of the annealed samples are consistent with a transformation into the quasicrystalline phase. This is also consistent with XRD results obtained from Technology Assessment & Transfer on coatings from runs 1060 and 1061.

The electrical resistivity of as-deposited and annealed AlCuFe coatings on alumina tribo flats coated during runs 1058, 1074, and 1075 are presented in Figure 20. The 1058A sample was annealed along with the 1060 and 1061 samples described previously. Although this coating shouldn't anneal into the quasicrystalline state, the electrical resistivity still increases due to the annealing process, although only by a factor of about 4 rather than the factor of 10 increase seen on the 1060 and 1061 samples. The electrical resistivity of the 1075 coating on the tribo flat that went through the heating cycles in the vacuum tribometer only increases to 1.6 mΩ cm. This supports the theory that the temperature of the 1075 pin/flat wasn't getting high enough to anneal the sample into the quasicrystalline phase during the heating process while collecting friction data. It is surprising that the resistivity of the 1074 flat is only about 1.5 mΩ cm after annealing, since there is XRD evidence that shows the 1074 coatings anneal to the quasicrystalline phase. This remains unexplained.

4.0 CONCLUSIONS

Vacuum tribometry of sputtered (as-deposited and annealed) 8 – 10 micron AlCuFe coatings on alumina has been performed on two pin/flat samples. One of these sets (1058) shouldn't convert to the quasicrystalline phase after annealing, whereas the other (1075) should. Since the temperature of the pin/flat interface only gets to about 200 C during the friction measurement the annealing process is incomplete. The tribometric behavior of these samples in the as-deposited state is qualitatively similar. The COF is ~0.5 at room temperature and decreases to ~0.25 at about 200C. We are unable to make a direct comparison between the tribometric properties of crystalline and quasicrystalline AlCuFe coatings.

The reflectance of as-deposited and annealed AlCuFe coatings has been measured from 0.28 – 26 microns. The reflectance of the annealed samples is relatively constant across the wavelength range at about 0.5 – 0.6.

The DC electrical resistivity of as-deposited and annealed AlCuFe coatings has been measured using a 4-point probe. The electrical resistivity increases by about a factor of 10 to about 2.5 mΩ cm for the 1060 and 1061 AlCuFe coatings on one inch diameter alumina disks. This is consistent with a transformation of the coating into the quasicrystalline phase and is in agreement with XRD results.

5.0 RESEARCH PERSONNEL

The work has been performed by members of the tribology team directed by Kurt Ketola (ksketola@raytheon.com, (310) 647-4393, (310) 647-4378 FAX). Bruce Buller, Geoff Nash, Lillian Hunter, and Norm Harris assisted in annealing the samples and performing the measurements. Dr. Michael N. Gardos was the original principal investigator for this contract and provided invaluable guidance and insight.

6.0 TRANSITIONS

Some of this work will be presented as part of a paper given by Larry Fehrenbacher of Technology Assessment & Transfer in a session honoring Mike Gardos at an upcoming STLE conference. Most of this work was presented at the Tribology Program Review held at the Naval Academy in Annapolis, Maryland on 4-5 June 2002.

7.0 REFERENCES

1. M.N. Gardos, "Surface-chemistry-driven Tribological Fundamentals of Diamond and SiC for Extreme Environment MEMS Applications," Progress Report for the Period 01 August 1999 to 31 July 2000, AFOSR Contract No. FA9620-98-C-0009, Raytheon Systems Company, El Segundo, CA 90245, 30 August 2000.

2. Z.M. Stadnik (Editor), "Physical Properties of Quasicrystals", Springer-Verlag, p. 405 (1999).

3. Z.M. Stadnik (Editor), "Physical Properties of Quasicrystals", Springer-Verlag, p. 131 (1999).

FIGURES

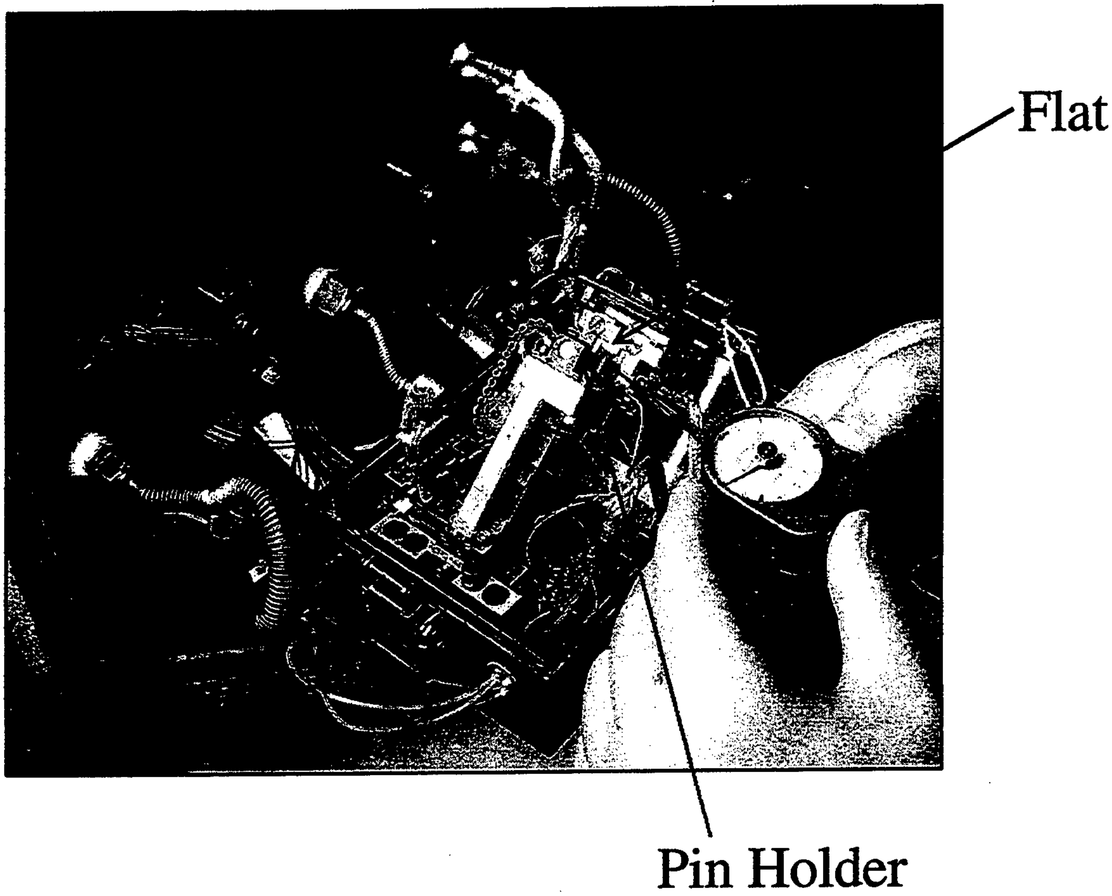


Figure 1: Pin-on-Flat Vacuum Tribometer

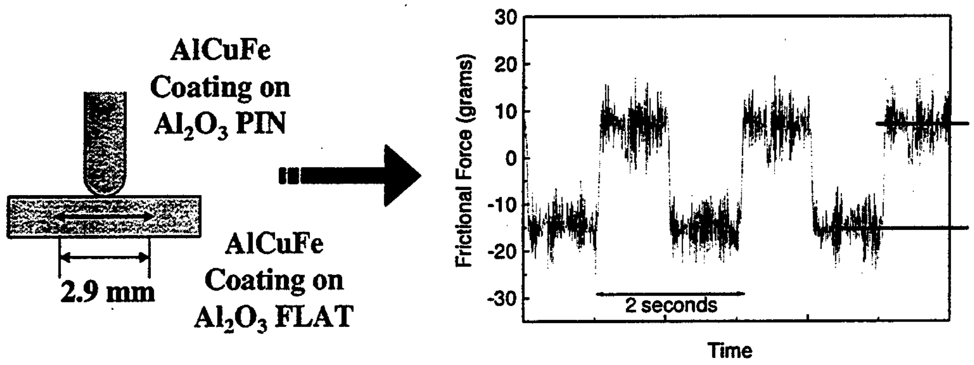


Figure 2: Pin-on-Flat geometry and raw frictional force data vs. time.

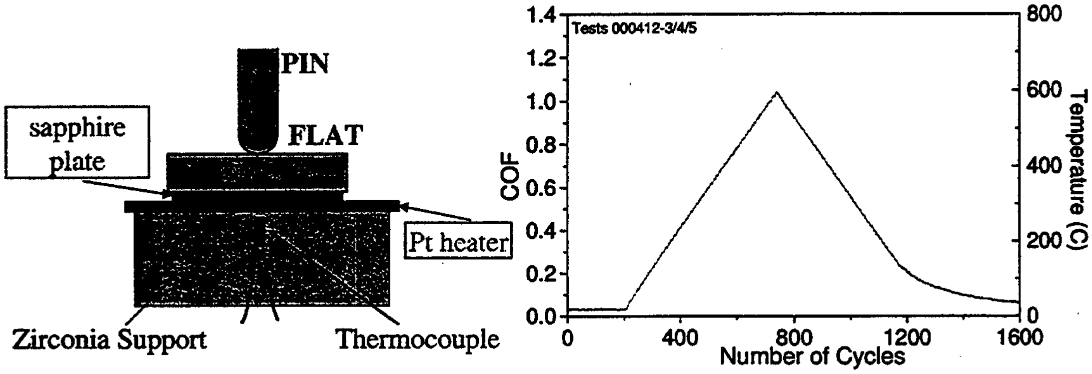


Figure 3: Detailed view of pin and flat showing location of primary thermocouple and heater. Standard heating protocol is shown on right. Friction data is collected for 200 cycles at room temperature, then the temperature is ramped at 35C/min to a maximum temperature of 600C. Then the temperature is ramped back down to near room temperature also at about 35C/min.

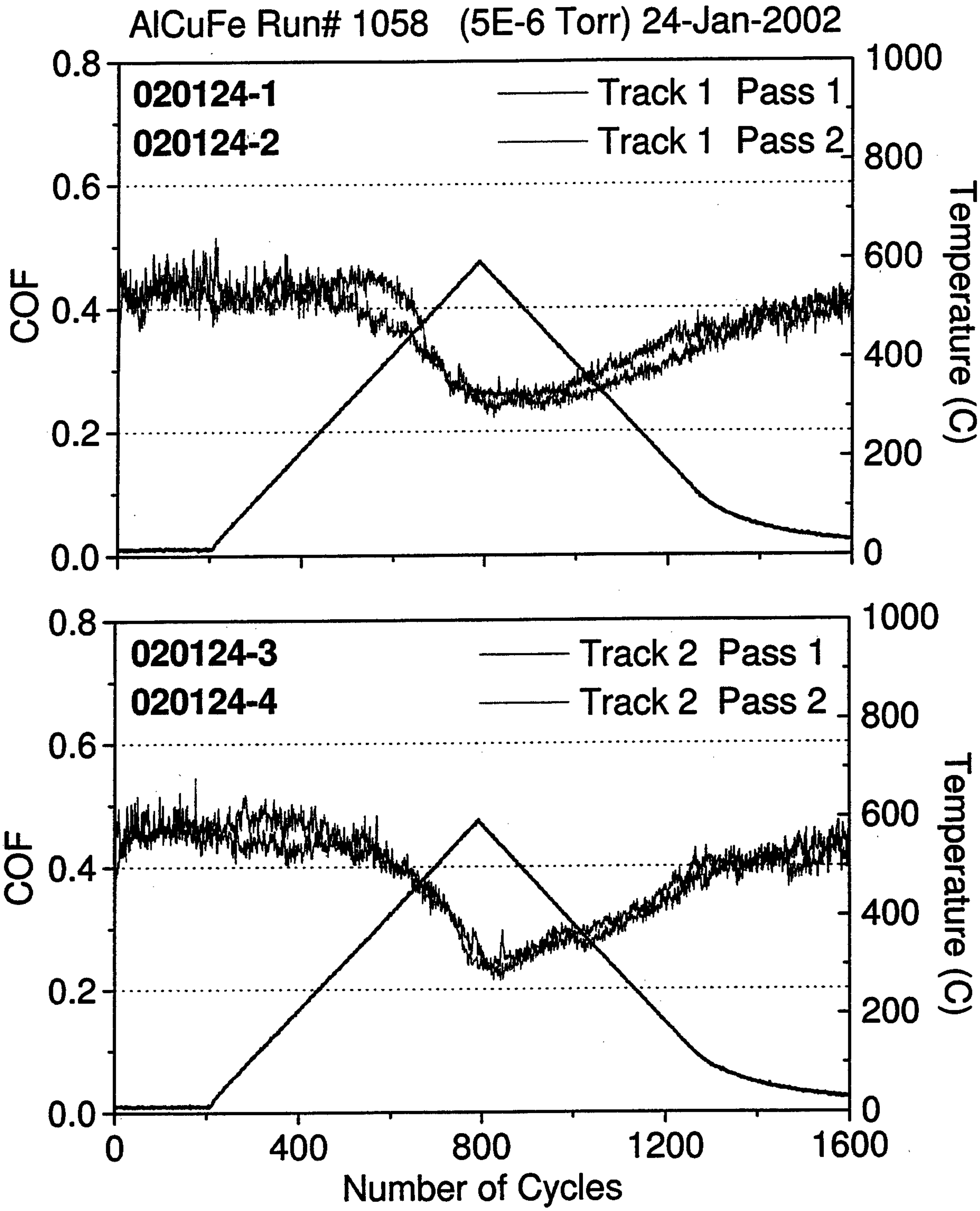


Figure 4: Coefficient of Friction vs. cycle number during heating and cooling ramps. Alumina pin and flat were coated with AlCuFe during sputtering run number 1058. The red curve shows the temperature of the thermocouple located below the heater as a function of the cycle number. The vacuum chamber is vented and the flat is moved slightly so that the pin will form a new wear track during the next two experiments.

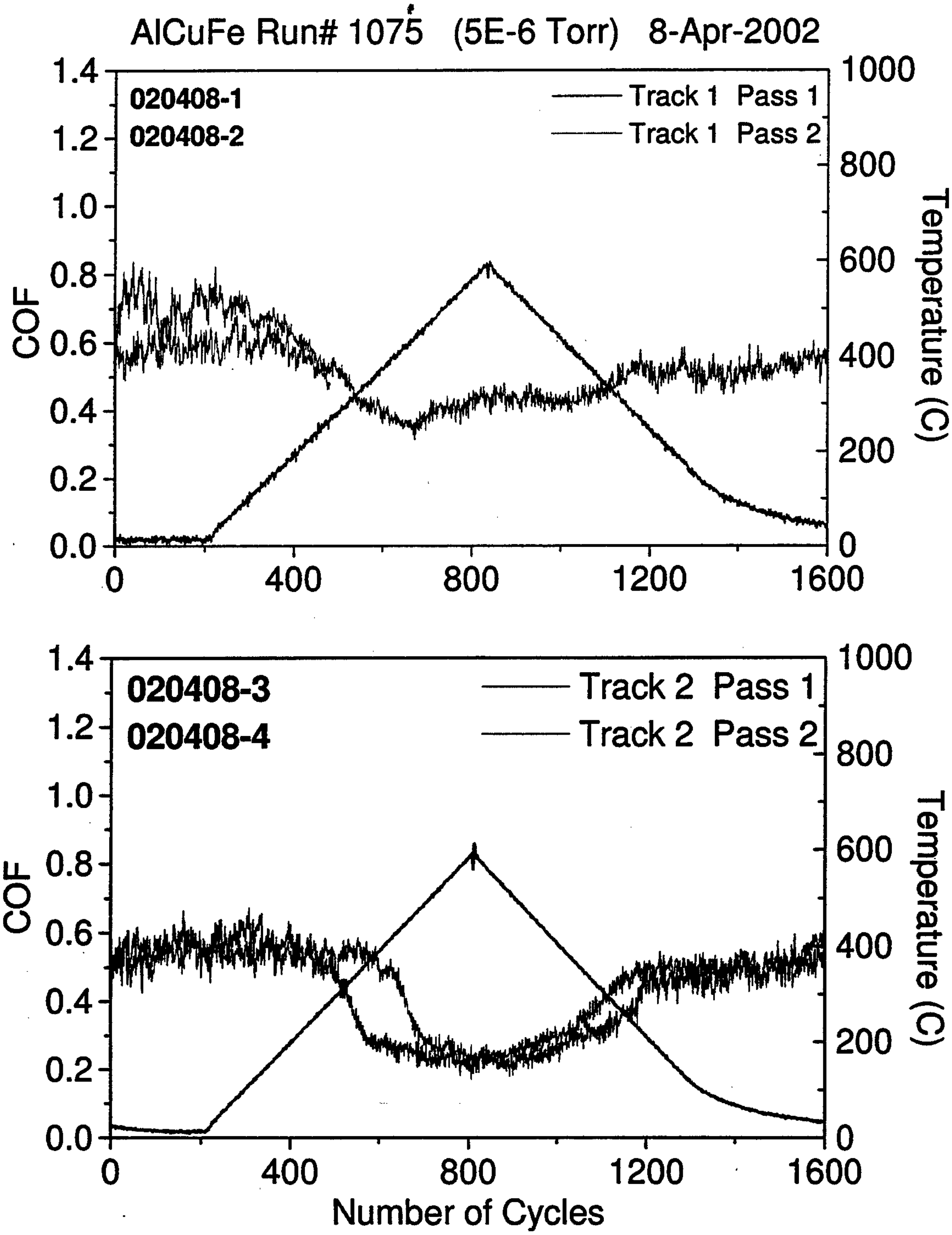


Figure 5: Coefficient of Friction vs. cycle number during heating and cooling ramps under vacuum. Alumina pin and flat were coated with AlCuFe during sputtering run number 1075. The heater was damaged during the Track 1 Pass 2 test which caused the test to be terminated.

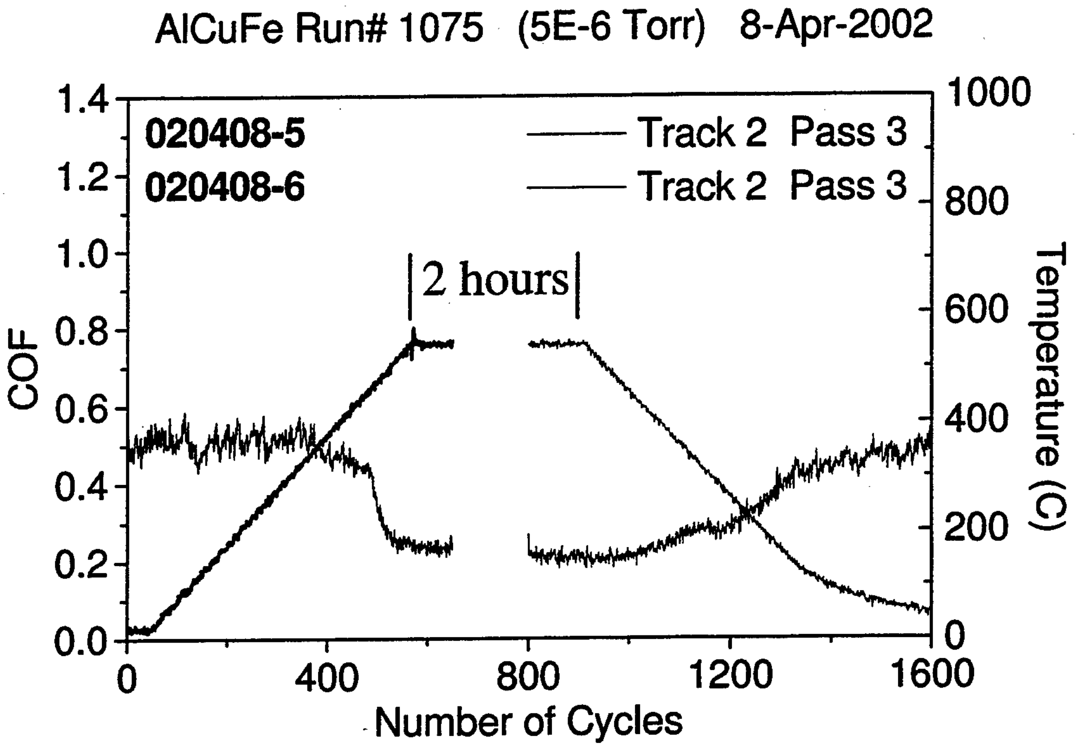


Figure 6: Track 2 Pass 3 friction data vs. cycle number. In this case, the pin-on flat oscillation is stopped shortly after the thermocouple temperature reaches the maximum of 600C. The temperature of the thermocouple is held constant for about two hours and then the pin-on-flat oscillation is started up again and friction data is once again collected while the temperature is ramped back down to room temperature.

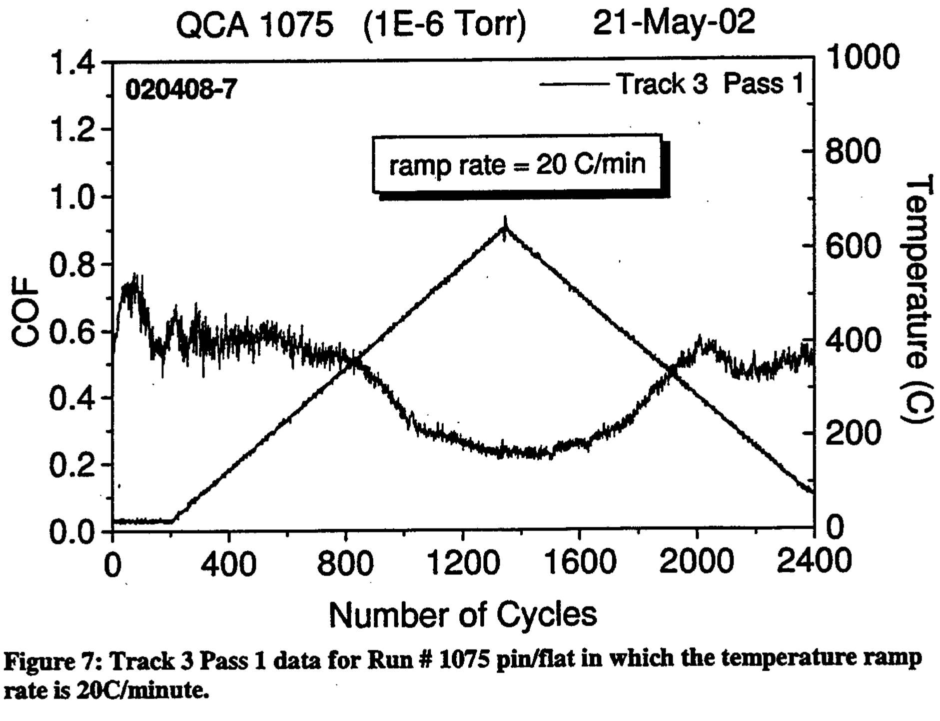


Figure 7: Track 3 Pass 1 data for Run # 1075 pin/flat in which the temperature ramp rate is 20C/minute.

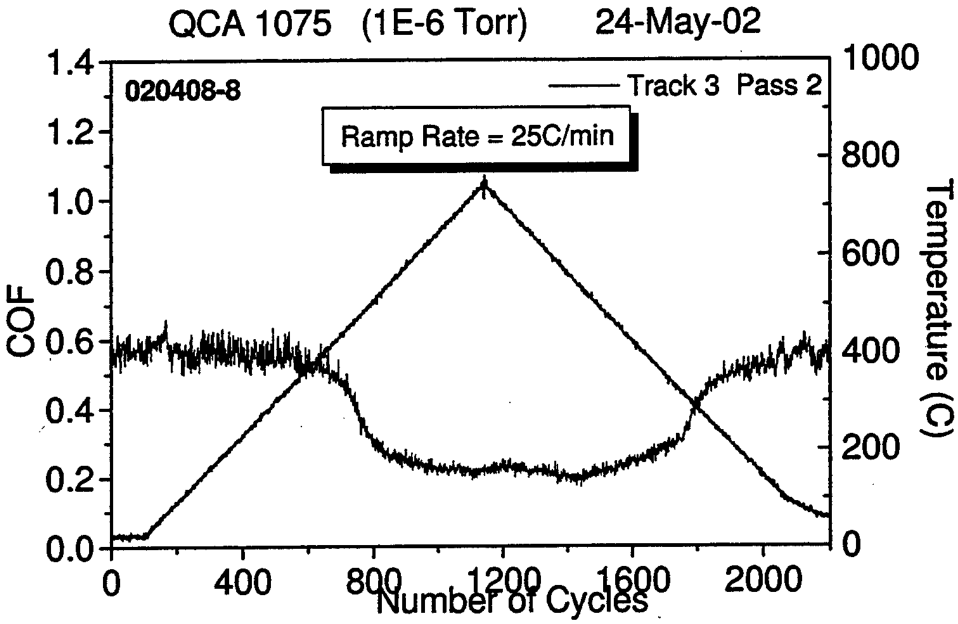


Figure 8: Track 3 Pass 2 data for Run # 1075 pin/flat in which the temperature ramp rate is 25C/minute.

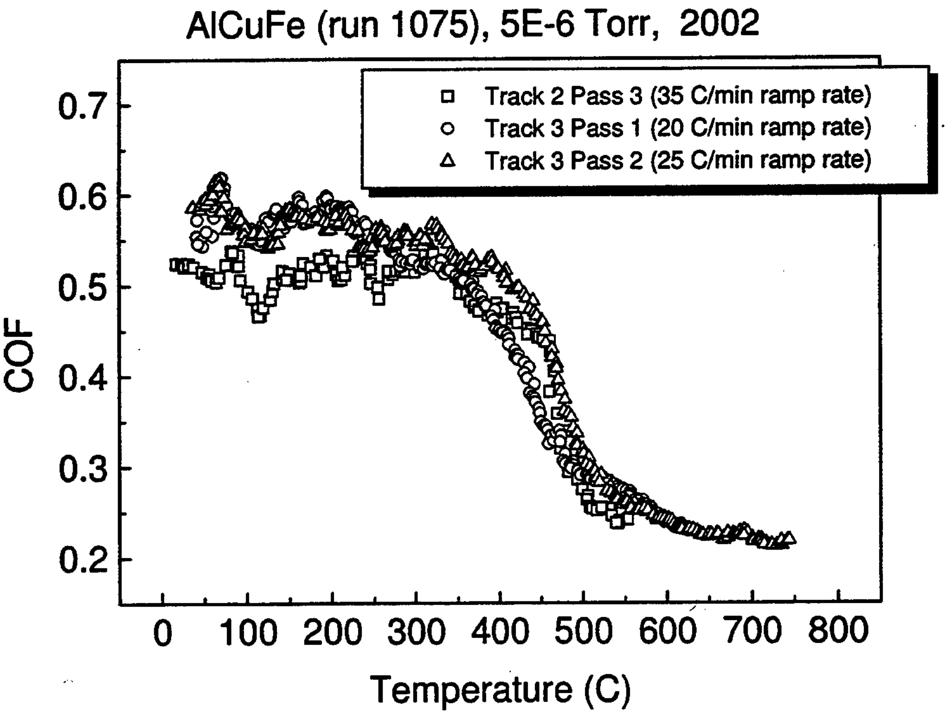


Figure 9: Coefficient of Friction vs. thermocouple temperature for three different temperature ramp rates. Changing the ramp rate doesn't appear to have any effect on the COF vs. temperature behavior.

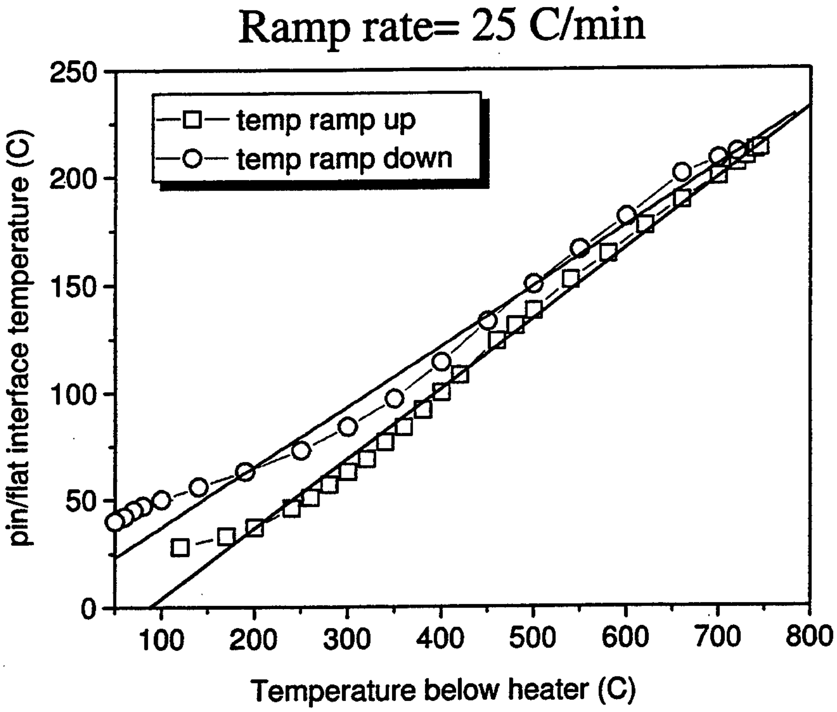


Figure 10: Temperature of a thermocouple squeezed between the pin and the flat (no relative motion) vs. the temperature of the thermocouple below the heater. The pin/flat interface temperature is considerably lower than the temperature of the thermocouple located below the heater.

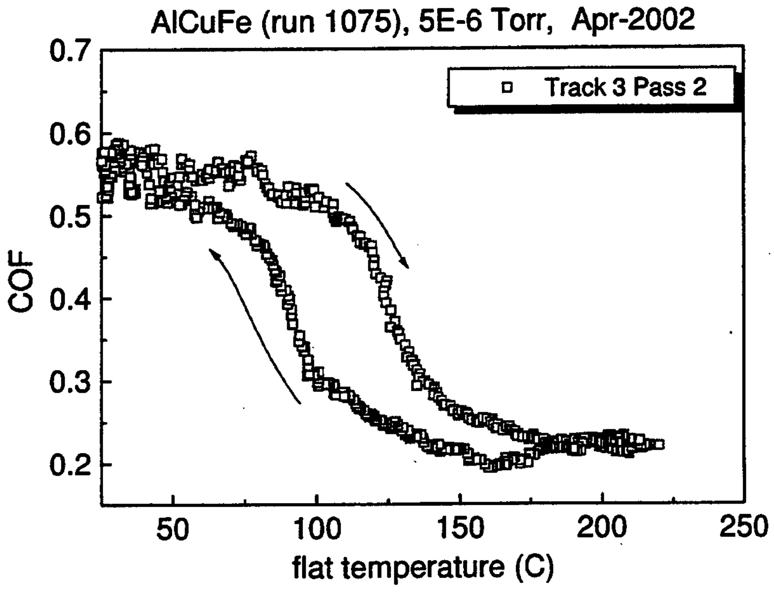
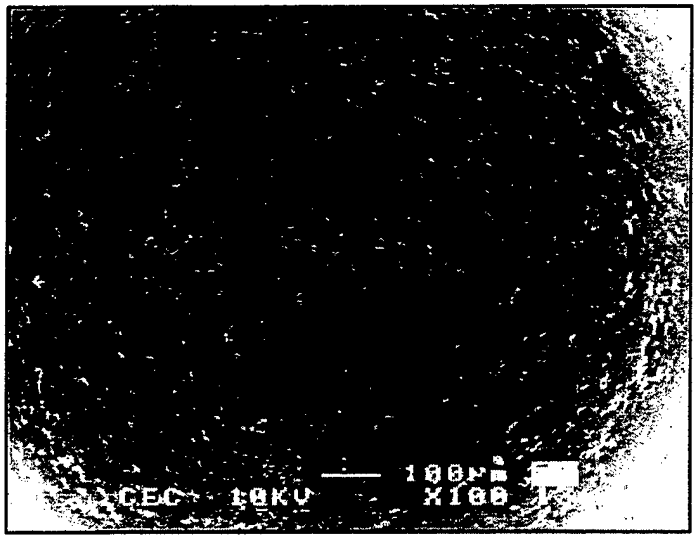
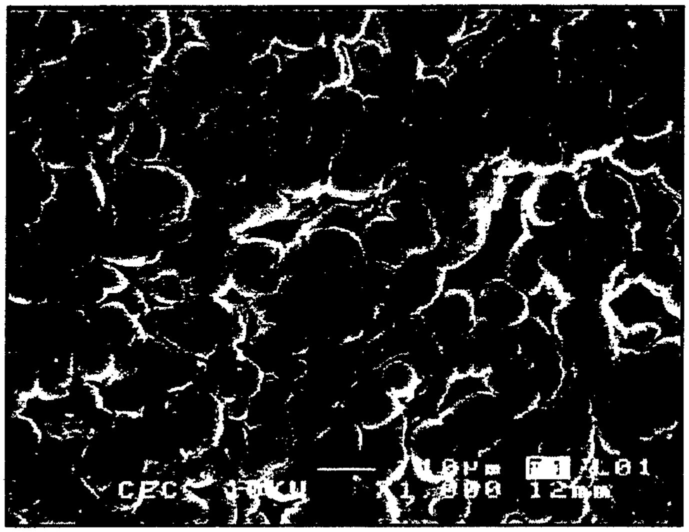


Figure 11: COF vs pin/flat interface temperature estimated from the data in Figure 10.

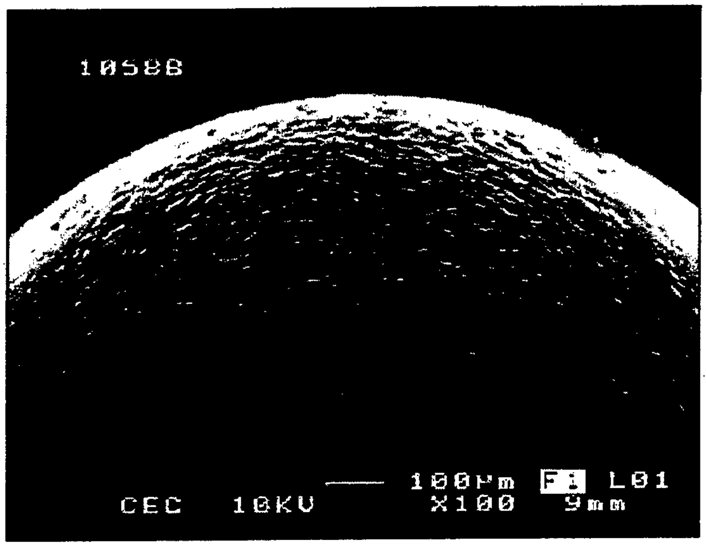


Pin 1075 as-received

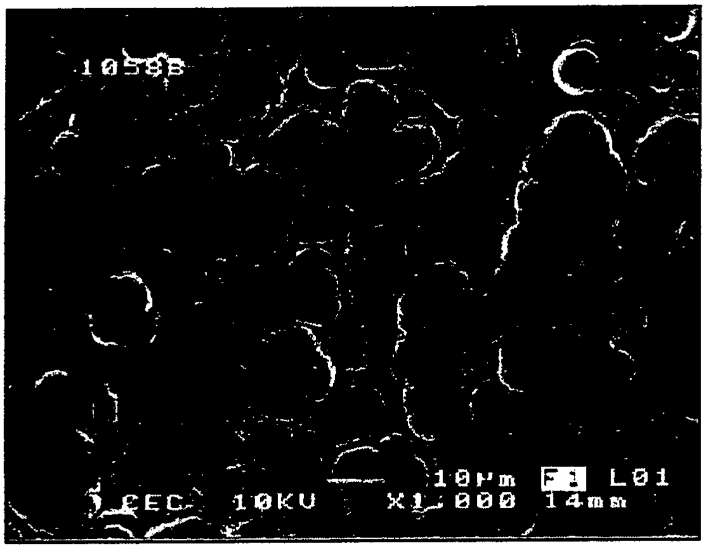


Flat 1075 as-received

Figure 12: SEM photos of pin/flat 1075 as received.



Pin 1058 as-received



Flat 1058 as-received

Figure 13: SEM photos of pin/flat 1058 as received.

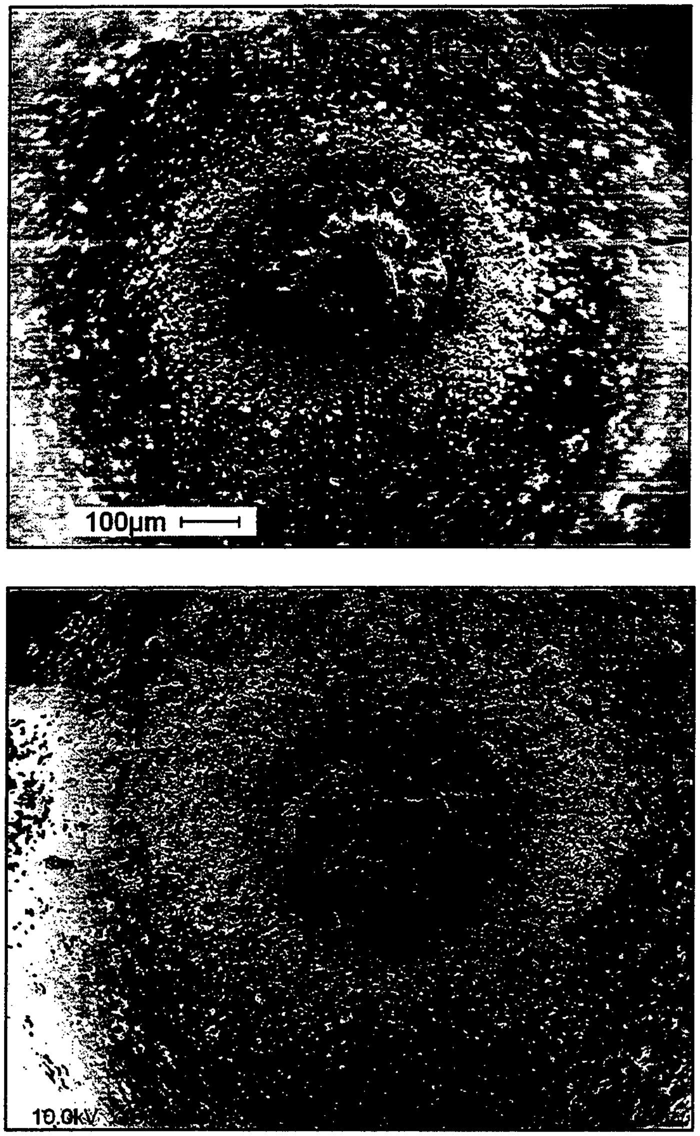
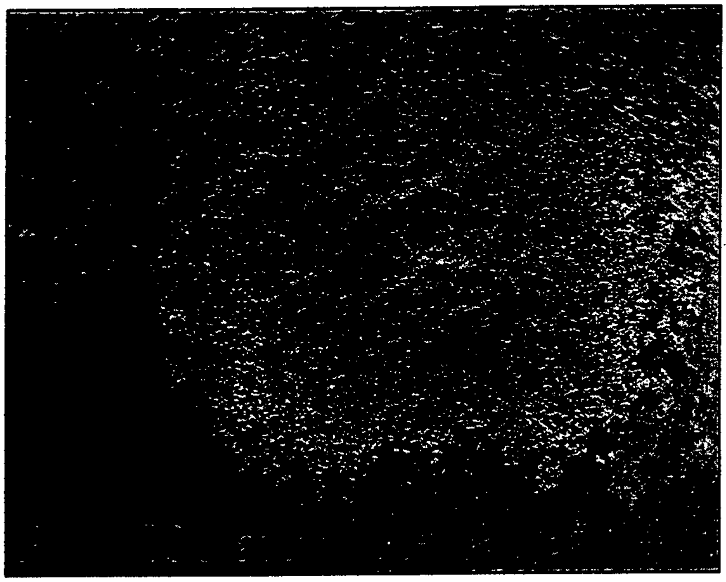
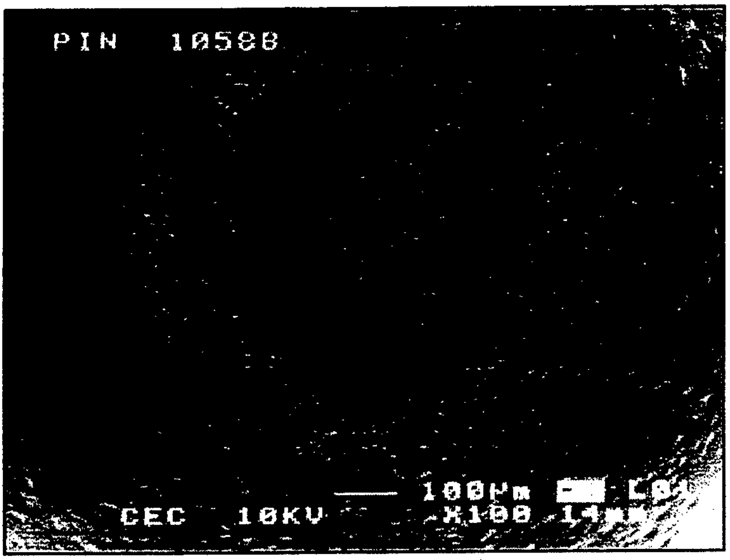


Figure 14: SEM photos of the tip of pin 1075 after two tests and after 5 tests. The calculated wear rate is 7E-12 m^{3} N^{-1} m^{-}





Pin 1058 after 4 tests

Figure 15: SEM photos of tip of pin 1058 after two tests and after 4 tests. The calculated wear rate is 7E-12 m^3 N^{-1} m^{-1}.

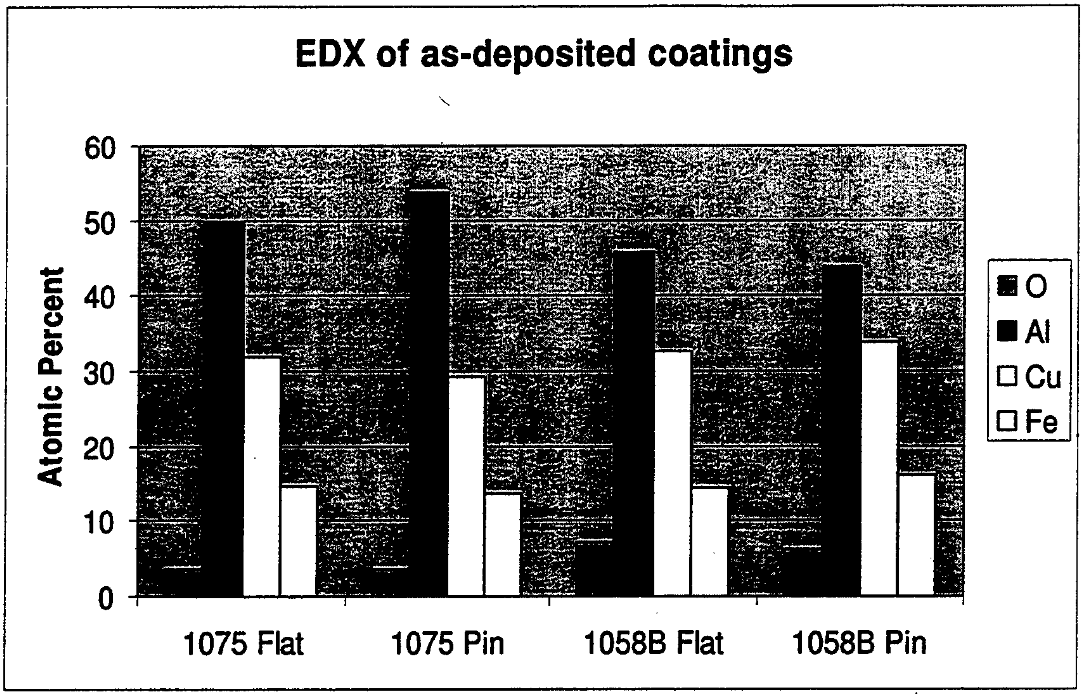


Figure 16: EDX analysis of 1058 and 1075 pin/flats.

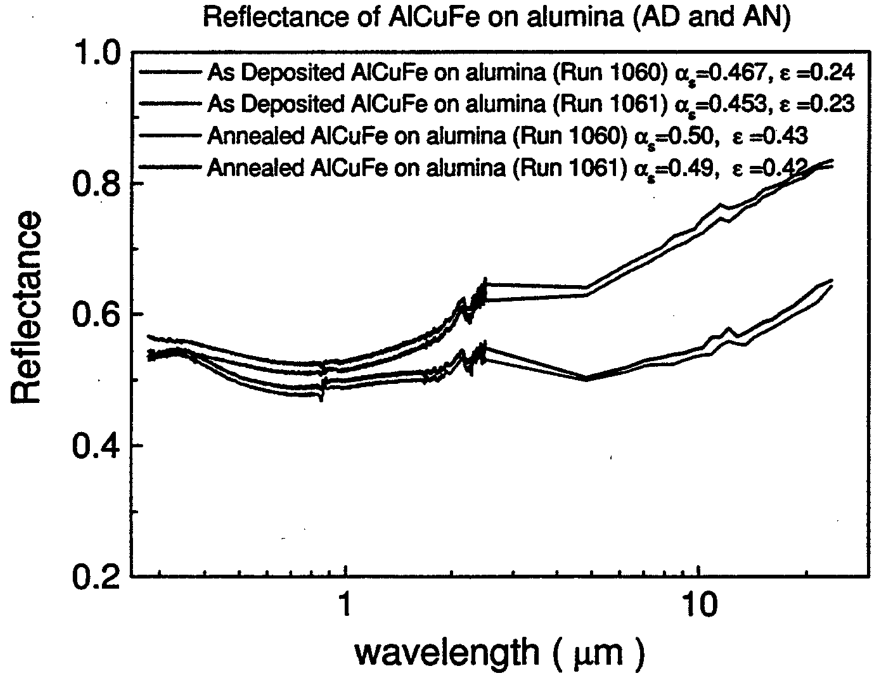


Figure 17: Reflectance of as deposited (AD) and annealed (AN) AlCuFe films on alumina substrates.

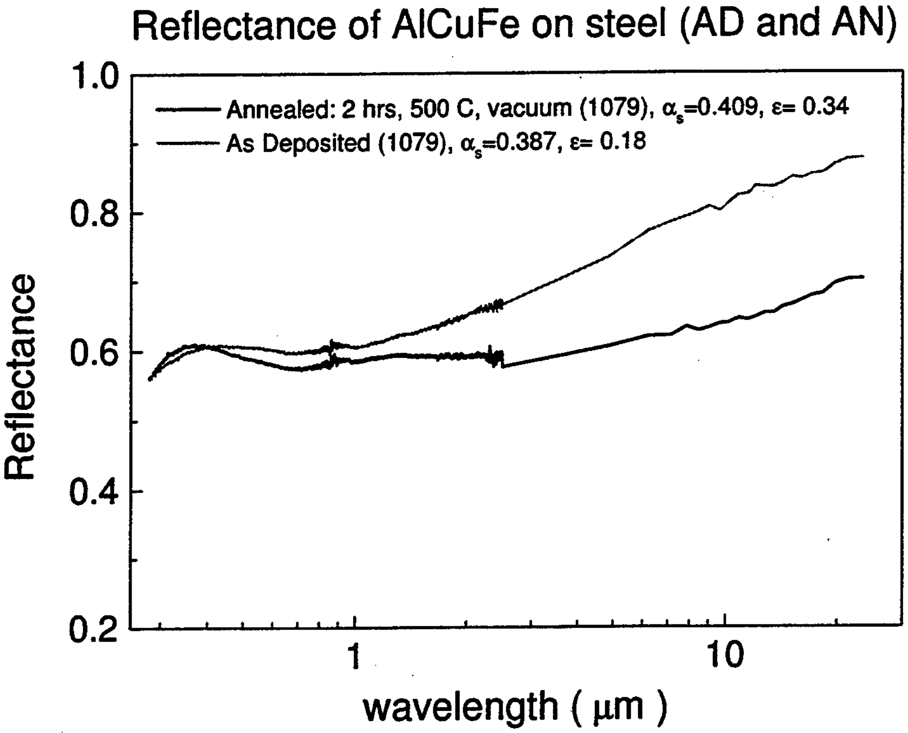


Figure 18: Reflectance of as-deposited and annealed AlCuFe on steel substrates.

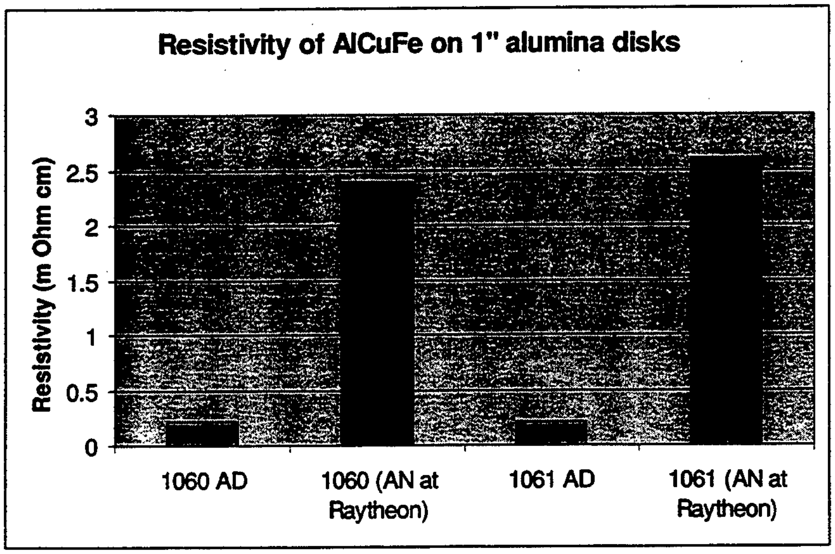


Figure 19: Resistivity of as-deposited and annealed AlCuFe films on one inch diameter alumina disks. Measurements are performed using a 4-point probe.

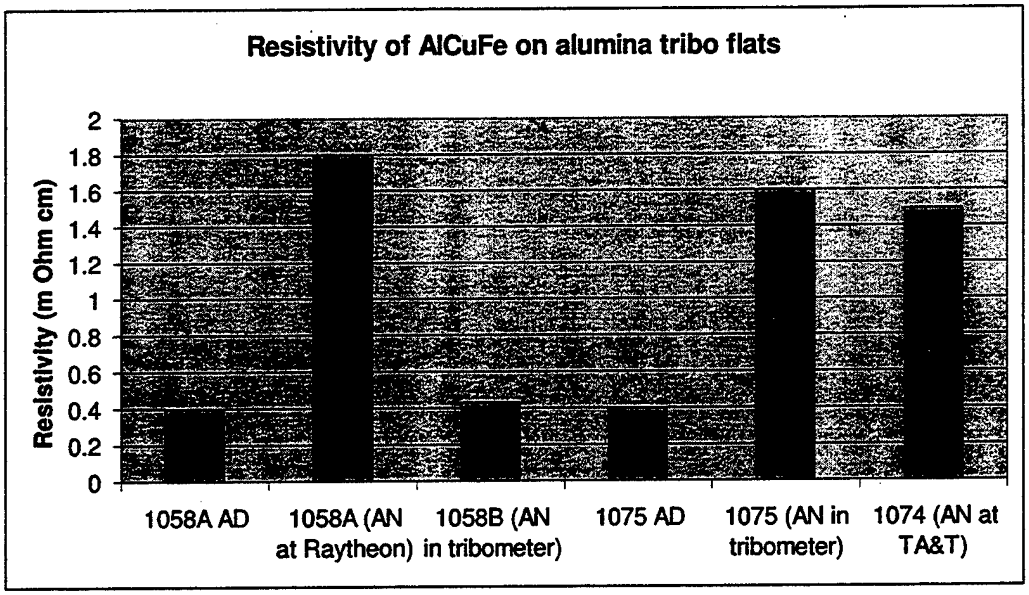


Figure 20: Resistivity of as-deposited and annealed AlCuFe films on alumina tribometry flats used in pin-on-flat experiments. Measurements are performed using a 4-point probe.