Adhesion, plasticity and other peculiar properties of solid methane

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Adhesion and plasticity of polycrystalline solid methane have been studied in the temperature range 10 – 90K. It was shown that adhesion is very strong in the 50K – 90K temperature range where the solid methane is soft and sticky. Closer to the melting point (at 90.6K) the solid methane behaves as extremely viscous non-Newtonian liquid. Below 30K solid methane loses its stickiness and ductility and acts like ordinary glass. Methane adhesion remains similar for very different materials. We have also made some video observations which reveal unexpected and mostly inexplicable properties of solid methane which could be of some interest for designing new methane moderators for neutron sources and planetary physics particularly the study of the environment of Titan.

Solid methane; adhesion; moderator.

1. Introduction

Methane is one of the most abundant hydrocarbon compounds known. It occurs widely in our environment in solid, liquid and gaseous forms both terrestrially and extra-terrestrially. On Earth, methane is the major constituent of natural gas [1] which is extracted from wells, then transported and stored in the liquid form, before being released as low pressure gas into the gas supply grid. There is also significant presence of methane on several planetary bodies in the solar system. The lakes of liquid methane and ethane on Titan, a moon of Saturn, have been detected by the *Cassini–Huygens* space probe, and had been suspected long before [2, 3]. Condensed methane (possibly crystalline) has been detected on Pluto [4] and Neptune moon Triton [5].

During last decade there is a growing interest in using solid methane as a moderator for a pulsed cold neutron sources, because from a neutronic point of view, this is the best moderator material known so far [6]. However designing a high cooling power cryogenic neutron moderator is extremely challenging engineering task, which requires a vast knowledge of solid methane thermodynamic and mechanical parameters. Unfortunately, despite few publications dedicated to mechanical properties of solid methane, the situation is still quite far from clear.

The first study of the mechanical properties of solid methane in tension [7] demonstrated purely elastic behaviour of polycrystalline solid methane sample below 20K. However at higher temperatures the sample response to stress becomes time dependent and could be better described as visco-elastic. Authors of similar study [8] came to similar conclusion that the solid methane shows ductile deformation above 45K at whole range of the strain rate, whereas below 15K it shows brittle failure. The deformation mode changes from ductile to brittle at a temperature of about 30K, and this boundary depends not only on temperature, but also on strain rate. At a temperature 77K which is not far from the melting point (~ 90.6 K) the solid methane behaves like very viscous non-Newtonian fluid [9]. The measurements of creep rate of solid methane [10] in the intermediate temperature range 25K < T < 65K demonstrates Arrhenius form of temperature dependence with an activation energy of ~ 300K – 400K. In the high temperature region the temperature dependence remain Arrhenius but with activation energy of ~ 1100K and the creep rate becomes very dependent on applied stress.

In our paper we are going to discuss results of our polycrystalline solid methane “poke” tests. In these tests we measured adhesion of solid methane to surfaces of three different materials and estimated the dynamic viscosity of methane at temperatures close to the melting point. We have also developed and used in our tests a video set-up which allows us to observe dynamic behaviour of solid methane such as quick solidification, reaction to mechanical impact and melting of solid methane sample in helium atmosphere (~ 1 bar).

2. Experimental technique and sample preparation

The experimental system consists of a standard top-loading cryostat [11] presented in Fig.1a with cryogenic insert (1) thermally attached to the cryocooler (2). The bottom part of the insert, which is connected to the 2nd stage of the cryocooler, forms a low temperature aluminium cell (3) where solid methane sample is produced. The central part of the insert, connected to 1st stage of the cryocooler (4), is always controlled at 115K in order to prevent methane from condensing and solidifying in this area. We also have thermometer and heater installed on the sample cell. The temperature of the cell can be controlled in temperature range 9K – 120K, with stability better than ± 100 mK.

In our experiments we use two different configurations of a sample stick compatible with the 50 mm diameter insert of the cryostat: “poke” test and “video” set-up styles. The “poke” test sample stick configuration is presented in Fig. 1b. Both configurations have got a bellows section (5) which allows vertical stick displacement ± 1cm without breaking the vacuum sealing of the insert which prevents a contact between the methane gas and atmospheric environment. An edge-welded bellows has been chosen because its mechanical resistance to the displacement of couple millimetres (from equilibrium position) is negligible in comparison with forces applied in experiment. The displacement sensor attached to the stick allows measurements of a few millimetres vertical displacement with 0.01 mm resolution. In case of the “poke” test configuration we have used 10 mm high and 10 mm diameter replaceable cylindrical probe (6) attached to the cylindrical copper block (7). A rhodium iron temperature sensor and standard heater are mounted on the copper block so that we can control the temperature of the probe independently of the insert. In our experiments we have used three geometrically identical probes made of different materials: aluminium alloy 5083, stainless steel 316 and PTFE.

The cylindrical shape DC electromagnet is attached to the top part of the stick. This set-up allows us to apply to the probe a vertical force pointing down by loading measured weight to the top of the electromagnet. This also gives us an opportunity to generate the vertical force pointed up. In the latter case the electromagnet (DC current is on) is in mechanical contact with a soft iron disk attached to a counterbalanced weight which pulls the probe up. This set-up also allows us to gradually increase the force.

As it is shown in Fig.2 (a, b, c) another, foot-shaped probe (2) is attached to the copper block (4) in the “video” configuration. This configuration also differs from “poke” test one by addition of optical-fibre borescope (5) fixed on the stick so the lens is vertically viewing (1) the edge of the foot. On the view from the borescope (1) photo in Fig.2 (c) we can see the end of the foot (2), and solid methane surface (3) which is usually placed few millimetres below the foot probe.

The methane gas of 99.95% grade purity (similar to one used in the methane moderator operation) is supplied from standard gas panel. After the temperature of the sample cell is stabilised at 110K we start to condense the methane gas into the insert. In our experiments we condense enough gas to provide ~1.5 cm deep liquid methane sample. After that the temperature of the insert is reduced to the temperature of interest where we wait for half an hour until thermal equilibrium between sample cell and probe is achieved. The pressure of methane vapour at temperatures below solidification is significantly less than atmospheric, which generates a compressing force which collapses unsupported bellows. We prevent this from happening by using restricting studs which keep the bellows stretched. After the temperature equilibrium is achieved we let helium gas into the insert, so helium pressure compensates the atmospheric pressure outside the bellows. After that the studs are removed and system is ready for measurements.

Initially the probe is gently moved towards the surface of the solid methane until it touches. After that the position of the displacement gage is zeroed and the helium pressure is adjusted to cancel the mechanical force caused by atmospheric/helium-gas pressure difference. After that we start recording the probe displacement as a function of time. The example of the data collected at 88K is presented in Fig.3. In this Figure we also give simultaneous time dependence of force applied to the probe divided by surface area of the probe. Immediately after beginning of the record, four aluminium cylinders each weighing exactly 50 grams, are loaded onto the electromagnet top surface. The instant just after loading the last mass is marked in the graph by point *A*. After that the system remains in this condition for 5 minutes. At point *B* the weight is removed and the electromagnet gets connected to the counterbalanced weight which pulls the probe up. The scan starts at point *C*. The probe starts to creep in up direction and at point *D* the bond established between solid methane surface and the probe breaks. In Fig. 4 we present the displacement under tension in more convenient scale. In this case the bond breaks at 0.048 MPa shear stress. In our experiment the breaking shear stress is recorded for different temperatures and different procedures of sample preparation.

3. Poke test results and discussion

Before starting the poke test measurement we enjoyed an opportunity to poke solid methane by pushing the stick by hand. According to hand-feel the methane sample felt soft and sticky at high temperature around 70K and a hard solid at low temperature ~20K. As it is possible to see in video-clip in Ref. [12] after we push the stick by hand into the solid methane it remains stuck for half a minute before it gets disconnected by spring force generated by compressed bellows. The shear stresses corresponded to breaking point of the bond between solid methane and aluminium probe for different temperatures is presented in Fig.5. Square data points represent experimental procedure where the bond between solid methane and probe is established at 70K and after that the temperature of the sample is changed to the temperature of interest, where it stays for half an hour before the breaking test is conducted. At temperature above 60K the bond breaks at shear stress ~ 0.1MPa. However below 50K the bond becomes unbreakable even if we apply maximum available shear stress 0.3MPa for 7min. At 50K and 40K we still can see small creeping, but at 30K and 20K displacement is undetectable within 0.01 mm resolution.

When bond formation and breaking is done at the same temperature (rhomb points), the situation is different. At temperatures more than 30K the breaking occurs at little bit lower level of shear stress than in first test above 50K. However below 30K the methane stickiness disappears and it is almost impossible to produce the bond between solid methane and probe any more. In some sense the solid methane sample behaves like unsettled epoxy glue at higher temperatures ≥40K and well polymerised epoxy at lower temperatures ≤ 20K. It is worth to mention that outcome of the breaking test is not reproducible if we try to re-establish the bond at the same temperature immediately after the breaking event. The properties of the methane surface seem to be significantly affected by the probe impact. In order to get reasonable reproducibility we decided to melt our sample each time after breaking by heating the cell up to 105K and after that re-solidify the sample before the new test.

In order to investigate material influence on solid methane adhesion we conducted the same measurements for probes made of three different materials: aluminium alloy 7075, stainless steel, and PTFE. The results of measurements presented in Fig.6 show no significant difference between three different probes, which allows us to suggest that solid methane adhesion does not depend on material. The average breaking point shear stresses at high temperature is about 0.06 MPa.

The probe displacement data collected during the process of producing the bond (presented in Fig.7) can be used for study of visco-elastic properties of solid methane at high temperatures. The temperature dependence of the probe displacement is very strong: total displacement of the probe at 88K is more than 2mm. The displacement rate is also time dependent which could support the suggestion that solid methane at temperature not far from the melting point behaves like very viscous non-Newtonian fluid [9].

Rough estimation of solid methane viscosity based on definition of dynamic viscosity μ: $\frac{F}{A} = \mu \cdot \frac{\partial u}{\partial y}$ where $\frac{F}{A}$ is shear stress, and $\frac{\partial u}{\partial y}$ is shear deformation (which can be measured in our video test) gives us $5 \cdot 10^7$ Pa·s at 80K which is comparable with estimation from Ref. [9]: $3 \cdot 10^8$ Pa·s at 77K obtained in similar kind of measurements. Our data also agrees well with suggestion that methane viscosity in this temperature range follows the Arrhenius law, but in our case the thermal activation energy is ~1300K, little bit higher than ~1100K given in [10].

4. Video test results

Visual observation of the sample turned out to be a quite informative way of studying solid methane properties in our case. The main advantage of this method is ability to observe the sample dynamically. Growth of solid methane sample which starts from cold wall of the sample cell in *Video Clip 1* happens with significant delay caused by low thermal conductivity of solid methane [13]. Distinguishing between solid and liquid phases is based on observation of ripples on the surface of liquid caused by mechanical vibrations generated by cryo-cooler. By the time the visible part of the sample is frozen the temperature of the wall is already below 70K. We are expecting that similar behaviour could happen in rapidly cooled neutron moderators where some liquid may still exist when the temperature of moderator wall is already below 70K. Another interesting outcome of this observation is that solidified methane surface is quite smooth and shiny.

In the *Video Clip 2 w*e can see imprint produced by poking the solid methane sample at 70K. The edges of the imprint are very well defined and clearly seen. The situation is quite different if temperature of the sample is close to the melting point. In this case as presented in *Video Clip 3* at temperature 89K methane behaves rather like a very viscous and sticky liquid. The sample is not homogeneous: more dense grains or crystallites of solid methane are clearly seen.

All previous video clips have been recorder at saturated pressure of methane which is so small at temperatures below melting point, that we can consider it as vacuum environment. We also recorded *Video Clips 4* and *5* with ~ 1 Bar (0.1 MPa) helium gas in the insert. In *Video Clip 4* the sample of solid methane has been grown in helium gas environment. The poking the sample in these conditions and temperature 80K produces imprint with different edges than in *Video Clip 2* resembling a “soufflé” with a thin crust on the surface.

In our final *Video Clip 5* we present an absolutely unexpected effect which at the moment we have no clear explanation for, but it could be related to sublimation of solid methane. In the beginning we have solid methane sample at 80K in helium gas environment. After that we start heating of the cell using the cell heater. After some time methane snowflakes start to fly above the sample surface and within tens of seconds the process achieves its climax which can be described as a local methane snow storm. The snowflakes are very sticky and pretty soon the lens of the endoscope becomes completely covered with methane snow. Little bit later, at higher temperature, the solid methane starts to melt and liquid come into view. The snow covered the lens also starts to melt and produces a droplet of liquid methane. Another unexpected observation is presence of intensive turbulent helium gas dynamics in relatively small sample space.

5. Implications of test results for design and operation of methane moderator

The experimental results discussed above allow us to shed light on some of the processes which take place in the solid methane moderator. During initial fast cooling of a moderator full of liquid methane the solidification process starts on cold surfaces of moderator wall or heat-exchanger. Very quickly the bond between surface and bulk methane becomes very strong independently on the material of the wall. When the temperature of the wall is below 50K the bond becomes unbreakable. However poor conductivity [13] which provides significant temperature gradient, minimises the pressure the walls of the moderator vessel are exposed to (caused by the thermal contraction of the bulk methane). As a result of the temperature gradient, a significant part of the bulk methane remains either in liquid or in visco-plastic state and can easily deform releasing the negative pressure produced by thermal contraction. However the situation is entirely different if we start warming up the solid methane moderator irradiated by fast neutrons at low temperatures. In this case the energy stored in the form of reactive species at low temperature is released at higher temperature by thermally activated diffusion and subsequent reaction [14]. If we start slowly warming up whole moderator, this effect can cause rapid spontaneous heating of solid methane at temperatures above 50K [10], which in combination with thermal expansion [15] might damage the moderator vessel. In order to avoid this situation we would suggest initial fast local heating of solid methane by warming up the moderator or internal heat exchanger wall. This should quickly warm up thin layer of solid methane located near the interface to high plasticity state or even melt it. At the same time most of the methane remains cold because of poor thermal conductivity of solid methane. After that one can start safe warming up of whole moderator. Once the self-accelerating heating temperature is achieved the pressure generated by the thermal expansion can be released by squeezing out of excess methane which is either in liquid or in high plasticity state.

6. Methane on Titan

As we can see in *Video Clips 4* and *5* the presence of gas atmosphere significantly changes processes of methane melting and solidification making it more complex and sensitive to environmental parameters. These experimental conditions are similar to the Titan environment where we also have coexistence of condensed methane with gas atmosphere of comparable pressure. The most impressive similarity from our point of view might be the thin crust observed on the surface of soft solid methane shown on *Video Clips 4*. As it follows from ref. [16] the Huygens probe has landed on a relatively soft solid surface and settled gradually by a few millimetres after landing. Force profile measured by the Huygens penetrometer suggests that the surface might be covered by a thin, firm crust. This similarity allows suggesting that solid methane and methane snow particularly may be an important component in the Titan planet surface environment.

Another point of interest was the specular reflection from Ontario Lacus detected in radar observation during December 2008 *Cassini* probe flyby. The reflection signal was so strong that it saturated the probe's receiver. The conclusion drawn from the strength of the reflection was that the lake level did not vary by more than 3 mm over 100 m wide reflecting area. From this it was assumed that surface winds in the area are minimal at that season and/or the lake fluid is more viscous than expected [17]. We would like to offer another possible explanation for this phenomenon. Following our observations, the optical properties of solid methane surface (close to the melting point) are quite close to the properties of liquid surface. We note that the viscosity of solid methane, even near the melting point, is many orders of magnitude higher, which might explain extraordinary smoothness of the surface.

Suggesting that the idea of solid methane presence on the surface of Titan is realistic, the properties of methane presented in this paper could be taken into consideration during planning of the next Titan TiME mission [18]. The TiME lake-lander will splashdown on one of Titan methane seas known as Ligeia Mare and will sail for three months taking measurements of its make-up. However if the part of the sea is solidified the lander will become stuck on the surface and more than 6 tonnes-force (for suggested ~ 1m^2 bottom surface area of the lender) would be required to disconnect the lander from the sea.

7. Conclusions

In our experiment we measured methane adhesion to different kinds of materials. This is very strong in the 50K – 90K temperature range where solid methane is soft and sticky. Methane adhesion to aluminium, stainless steel and PTFE is more or less the same. Closer to the melting point (at ~91K) the methane behaviour becomes similar to the behaviour of very viscous (and still very sticky) non-Newtonian liquid. Below 30K solid methane loses its stickiness and ductility and behaves more or less like a normal glass. We also made few video observations which reveal some unexpected and mostly inexplicable properties of solid methane which could be of some interest for designing new methane moderators for neutron sources and planetary physics particularly study of Titan's environment.

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Figure captures:

Fig.1 (a) top loading cryostat; (b) The "poke" test sample stick configuration.

Fig.2 Video configuration of the stick.

Fig.3 Probe displacement and shear stress as a function of time.

Fig.4 Probe displacement and shear stress as a function of time near bond breaking point.

Fig.5 Shear stresses corresponded to breaking point of the bond between solid methane and aluminium probe for different temperatures. Square data points represent bond established at 70K and breaking test conducted at temperature of interest. Rhomb points represent bond established and breaking test conducted at the same temperature.

Fig.6 Temperature dependence of shear stresses corresponding to the breaking point of the bond between solid methane and probe for different materials of the probe: rhomb data points - aluminium alloy 7075; square data points – stainless steel; triangle data points - PTFE.

Fig.7 The probe displacement as a function of time during establishing the bond at different temperatures.

Fig. 8 *Video Clips*

Figure 1

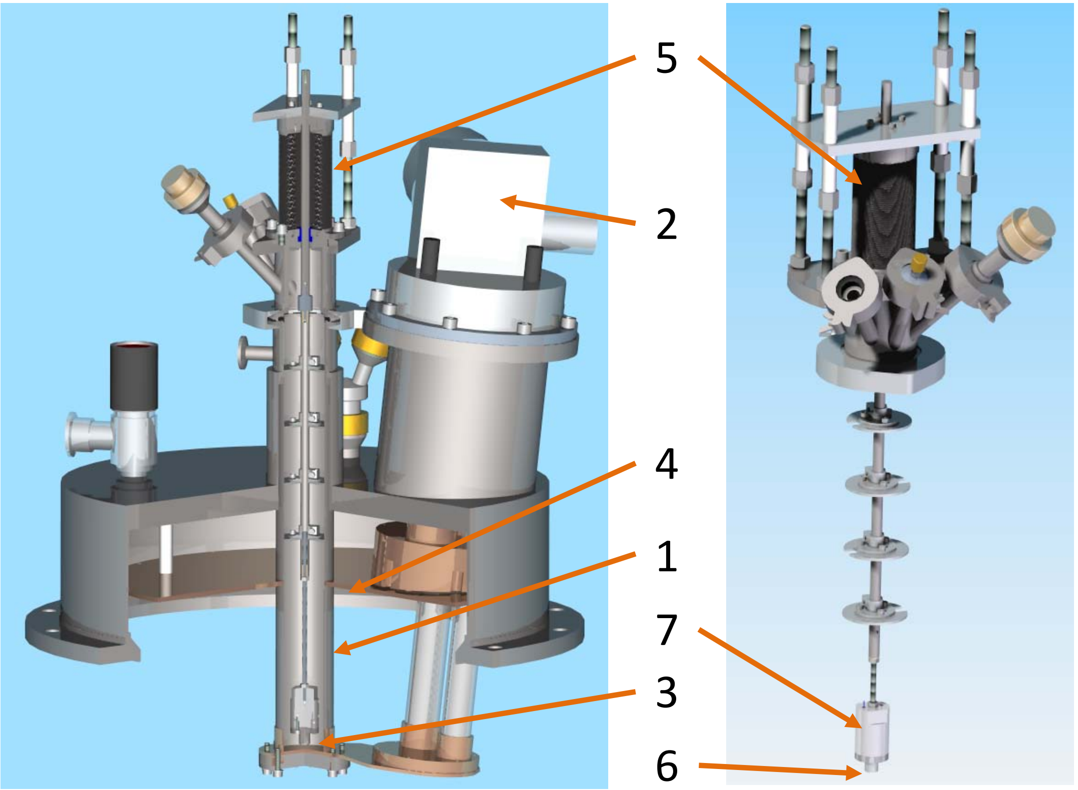


Figure 2

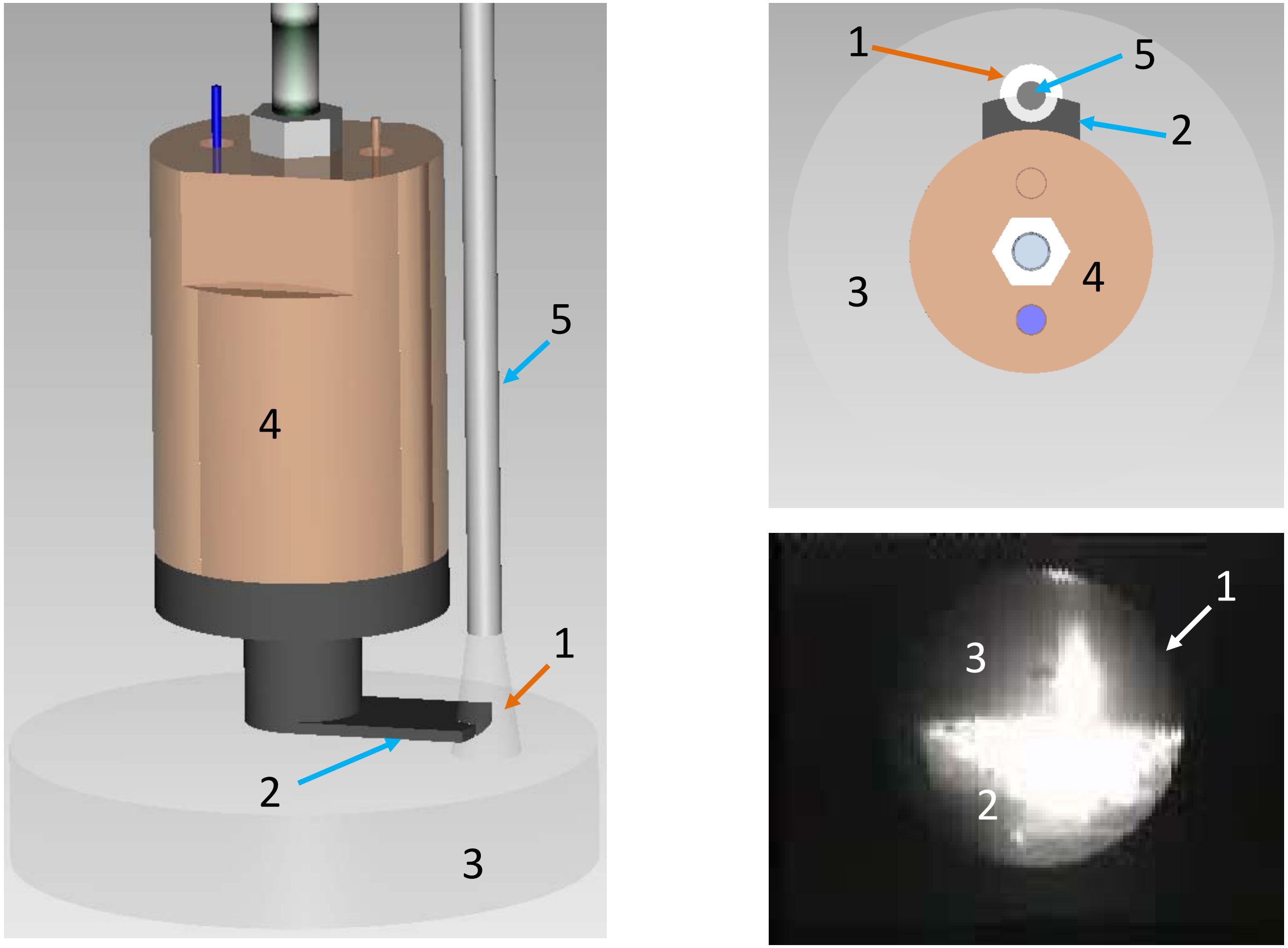


Figure 3

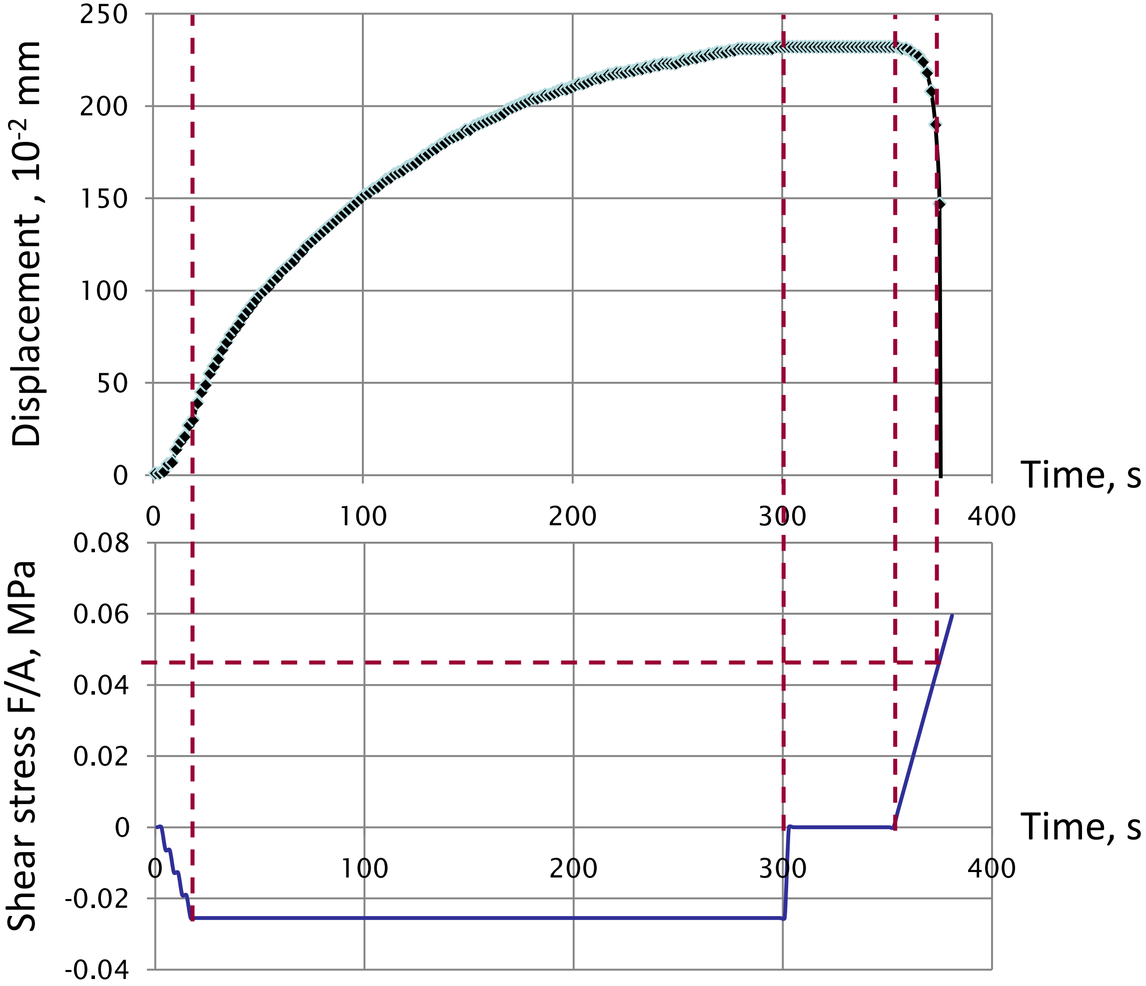
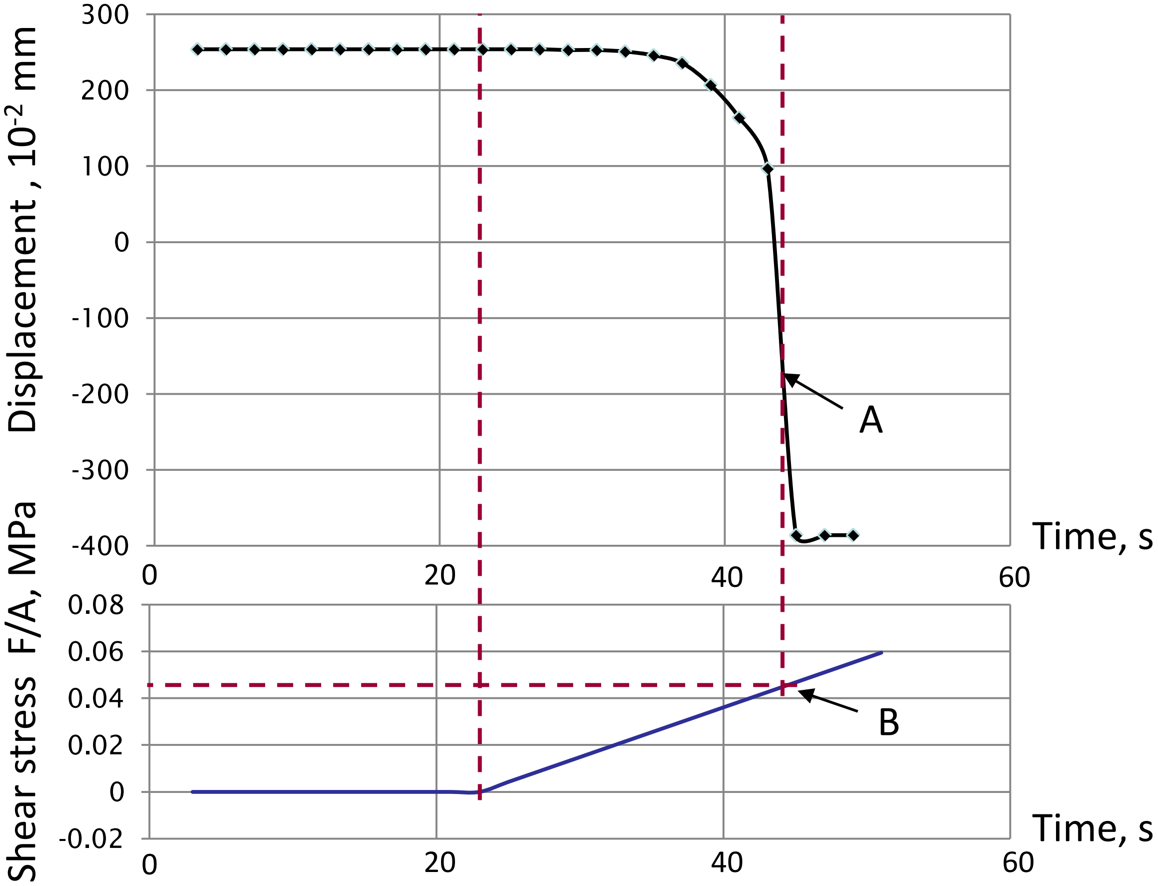

Displacement , 10^{-2} mm
250
200
150
100
50
0
Time, s
0
100
200
300
400
Shear stress F/A, MPa
0.08
0.06
0.04
0.02
0
-0.02
-0.04
Time, s
0
100
200
300
400

Figure 4



Displacement , 10^{-2} mm
300
200
100
0
-100
-200
-300
-400
0
20
40
60
Time, s
A
Shear stress F/A, MPa
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0
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0
20
40
60
Time, s
B

Figure 5

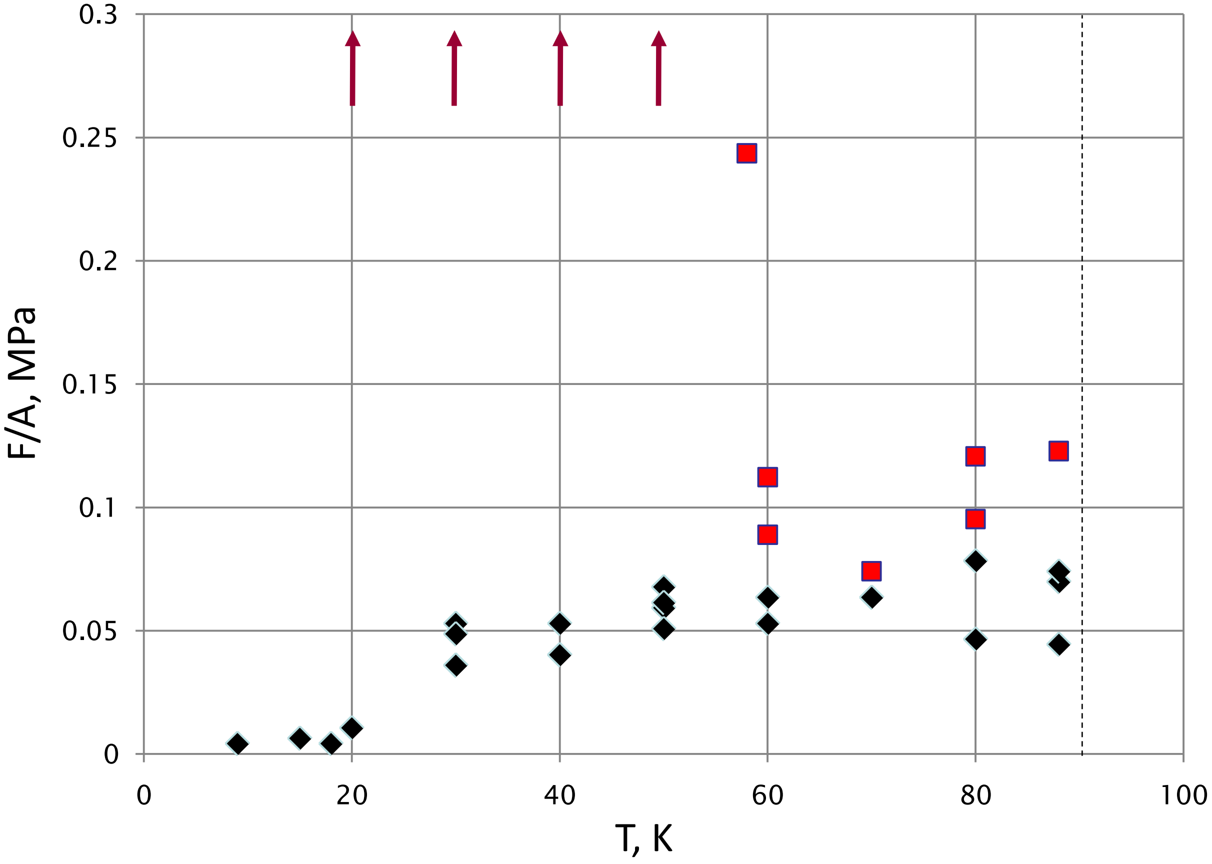

Figure 6

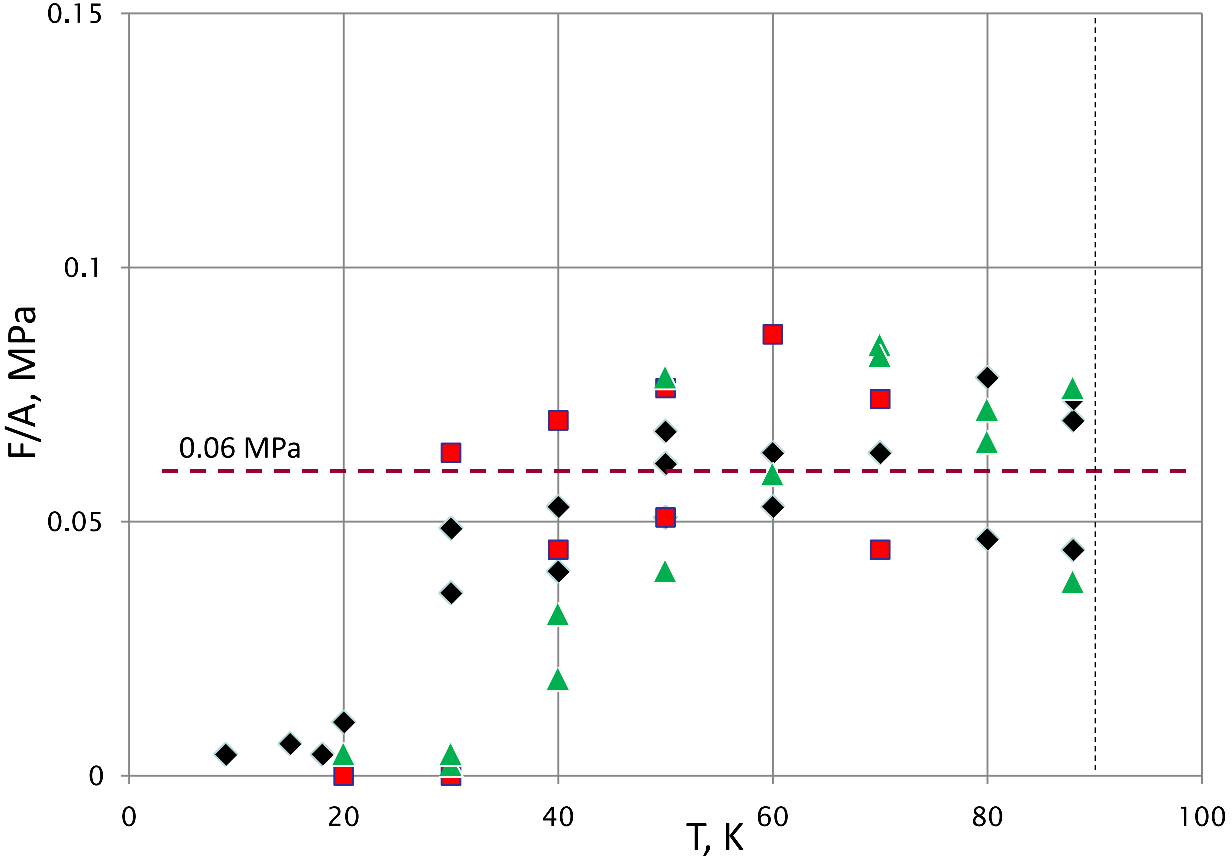

Figure 7

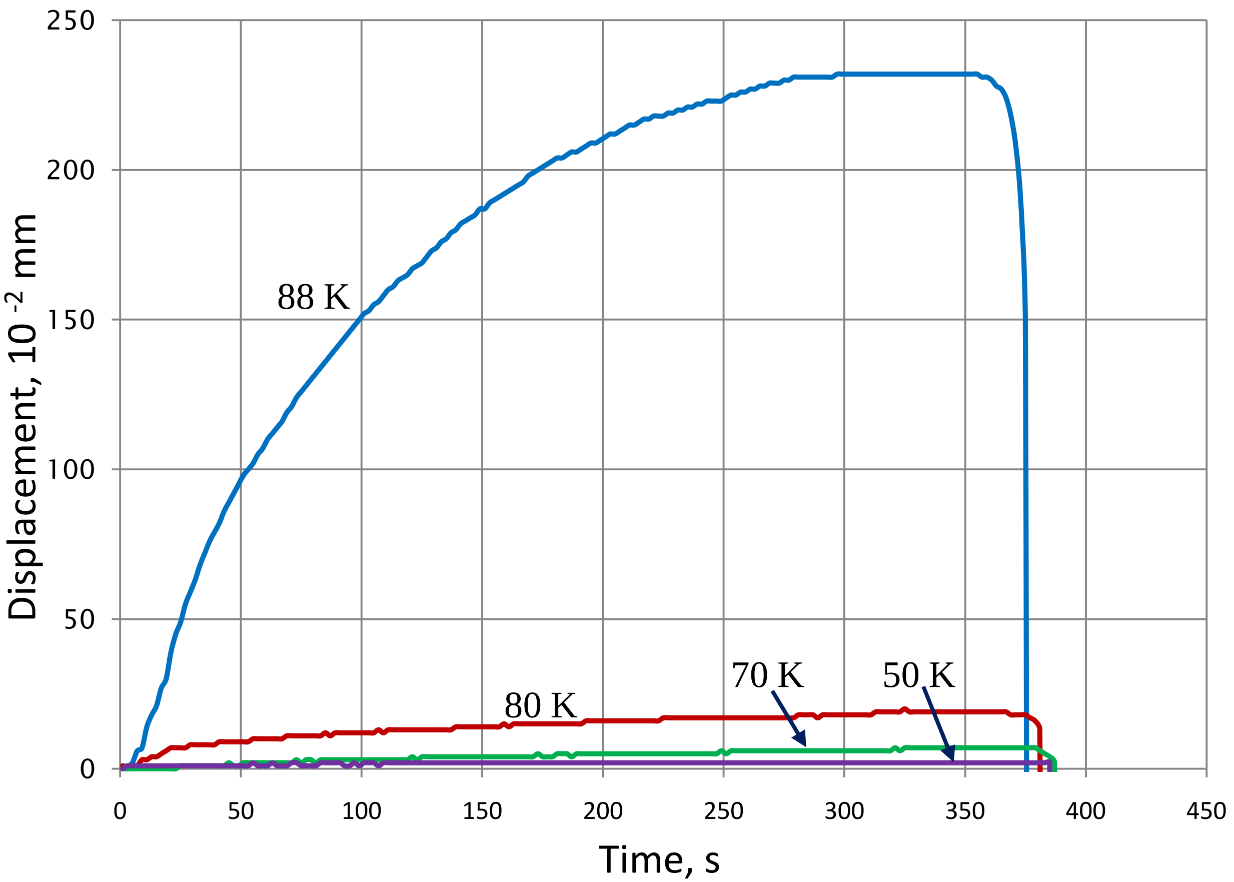
250
200
150
100
50
0
0
50
100
150
200
250
300
350
400
450
Displacement, 10 -2 mm
Time, s
88 K
80 K
70 K
50 K

Figure 8

Video Clip 1

Video Clip 2

Video Clip 3

Video Clip 4

Video Clip 5