Shear melting and high temperature embrittlement

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Temperature and heating in the shear band

Key to our mechanism is that the temperature in the shear band can rise to around 1400K in the timescale of the chip formation. It has been shown experimentally in metallic glasses that temperature increase can be as high as a few thousand Kelvin per nanosecond[1]. In that paper the temperature rise calculated in the adiabatic approximation, and was shown to be an order of magnitude larger than observed. Here we show that the length and time scales involved in machining lead to a rise in the shear band temperature to about the melting point. We will neglect geometric factors or temperature dependence of material properties and obtain of magnitude effects: it is not possible to predict precisely what the shear band temperature will be.

For our geometry, we assume that the shear band is a thin plate of thickness $l$, area $A$. The rate of energy production in the band is

$$\dot{Q} = \dot{\epsilon} \sigma Al/2,$$

with $\dot{\epsilon}$ the strain rate and $\sigma$ the yield stress. This expression was, in combination with the heat capacity, used as a test of our MD using temperature rise in an NVE ensemble.

The energy removed is calculated by assuming Fourier’s Law $\dot{q} = -kdT/dx$. This depends weakly on the temperature profile, but if we assume that $dT/dx$ is the temperature increase in the shear band divided by a diffusion length $d$ we find:

$$\dot{Q} = Ak(T_{\text{shear band}} - T_{\text{bulk}})/d$$

$k$ being the thermal conduction. In the steady state, these $\dot{Q}$’s are equal, so that

$$T_{\text{shear band}} = T_{\text{bulk}} + \dot{\epsilon} \sigma ld/2k$$

$\dot{\epsilon}$ is the strain rate within the shear band, rather than sample as a whole, so the parameter defining the experiment is $\dot{\epsilon}/l$ which, ignoring some geometric factors, should be equal to the cutting rate $V_c$. Using values of $v_c = 10\text{m/s}$; yield stress = 1GPa; $k = 22\text{W/m/K}$; $d=5\mu m$ gives an enhancement in temperature around 1000K, the same order of magnitude as required for melting.

We note the curious result that the steady state temperature is independent of the thickness of the shear bands (Lewandowski and Greer also commented on this).

This analysis assumes that the steady state can be reached in the timescale of fracture. The rate of temperature increase can be estimated by $\dot{T} = \dot{Q}/c_PV = \dot{\epsilon} \sigma /c_P$, where the specific heat capacity $c_P \approx 600\text{J/kg/K} (\approx 1 \times 10^6\text{J/m}^3/\text{K})$. This gives an adiabatic heating rate of order $10^9\text{K/s}$, so reaching the melting point would take of order $10^{-8}\text{sec}$.

These order of magnitude estimates show that at a cutting rate of $10\text{m/s}$, sufficient energy is supplied to melt shear bands of thickness $10^{-7}\text{m}$, and that the thermal conduction of titanium is such that for temperature differentials above 1000K the adiabatic approximation breaks down.

The dimensions of the MD simulation box are typically smaller than the shear band, so this temperature is represented by the thermostat in the simulations.

Despite the various approximations made, it is clear that, depending on material parameters, a shear band of micron thickness might generate enough heat to melt the sample: at that point the yield stress drops, and the heating is reduced. With reference to figure 3 we see the recrystallized shear band, is indeed about a micron across.

Samples and preparation

For sample preparation and machine testing, we used plasma arc melting to make several alloys based on Ti6Al4V and Ti15V3Al3Sn3Cr with rare-earth dispersoids (typically 0.9 wt.-%, in case of La additionally 1.4wt.-%, and 2.8wt.-%) of Ce (melting point=1071K) La (1191K) Nd (1294K) Y (1795K) and Er (1802K). The standard alloys were remelted to ensure consistent treatment.

For sample production, our machining experiments involved orthogonal high-speed cutting (to safely produce segmented chips in all alloys) on a modified grinding rotor[2], allowing cutting speed ($v_c$) between 5 m/s and 100 m/s at depth ($a_p$) between 0.05 mm and 0.2 mm, the length of cut was 50 mm. We also performed experiments using the "quick-stop" technique[2] (Supplementary Fig.4) at $v_c$ between 5 m/s and 20 m/s and $a_p$ between 0.05 mm and 0.2 mm to obtain root-chips[3, 4]. The length of cut was approx. 1 mm. Turning experiments at conventional cutting speeds of 1.3 m/s and cutting depths of 0.1 mm have been performed on a CNC (Computer Numerically Controlled) lathe to check the machinability of the modified alloys (e.g. Fig.2).

Metallographic cross sections have been prepared for all segmented chips and root-chips from the standard alloys which have been analysed by OM and FE-SEM. Selected samples of Ti6Al4V alloy were further analysed using TEM including selected area diffraction, which reveals localized shear bands and nano-crystalline microstructure (Fig. 2).
FE-SEM shear band analyses were sufficient to resolve the microstructure in Ti15V 3Al 3Sn 3Cr chips. Chips from conventional turning experiments have been analysed directly by means of SEM (Supplementary Fig.6).

The preparation of metallurgical cross sections of REM-containing Ti6Al4V chips has been impossible due to chip fragmentation: Chips coming from the orthogonal cutting and quick-stop experiments were extremely fragile and either lost during cutting or separated into individual segments if not already fully fragmented. The chips coming from the turning experiments on the other hand were too curved for TEM sample preparation, and fragmented when straightened.

We performed orthogonal high-speed cutting and quick-stop micromachining experiments [2] which allow for subsequent analysis of chips and root-chips. In addition, we performed turning experiments with state-of-the-art cutting parameters. For cutting speeds \( v_c \) between 5 m/s and 100 m/s we find that Ti6Al4V alloys containing Ce, La and Nd undergo the shear-band transformation and the chips fragment, whereas those containing Y and Er do not (Supplementary Fig.3). This correlates with melting point as expected. However, REMs in Ti15V 3Al3Sn3Cr alloys did not produce the same effect. X-ray diffraction of these materials revealed that instead of REM dispersoids, stable intermetallics like La5Sn3 formed (Supplementary Fig.5). These have high eutectic points and so the eutectic mixing is actually suppressed and no fragmentation occurs.

X-ray phase analyses on the new alloys have been performed using synchrotron radiation at DORIS, BW5, and PETRA III, P07. We used synchrotron radiation to probe the bulk, because REMs are air-sensitive and would oxidize if exposed to air, and because the particle volume fraction is too low for conventional X-ray diffraction. We used energies between 75 keV and 100 keV, beam size 0.25 mm \( \times \) 0.25 mm and 0.5 mm \( \times \) 0.5 mm. Bulk samples of approx. 10 mm thickness have been analysed in transmission, the recorded patterns have been integrated by the Fit2D software and analysed with the CMPR software package together with the PDF2 database (release 2005)[5, 6]. In addition to phase analysis, we also used focused X-ray methods, illuminating (transmission mode) for 0.5 s by a focused 80.09 keV beam (2.2 \( \mu \)m \( \times \) 34 \( \mu \)m) at room temperature.

**Mechanical Properties of REM-containing alloys**

For practical applications, it is important that the REMs do not have serious adverse effects under ambient conditions. The addition of Yttrium [1] or neodymium [2] to titanium alloys is known to lead to embrittlement and reduced the ductility of related alloys. Cerium has a low melting point and can melt during forging. The other potential pitfall is the formation of hard intermetallics such as La5Sn3.

Therefore, for practical application, we minimize the La and Nd contents. 0.9% of lanthanum are needed to reduce the chip length in conventional machining sufficiently that the chip fragments can be removed from a hole (deep-hole drilling) with cooling liquids, and turning processes can be automated without interruptions to remove the chips. Increased embrittlement is measurable in Ti6Al4V 0.9La, but much less pronounced compared to the earlier studies on titanium + yttrium. In general, higher lanthanum contents lead to lower ductility as expected.

We have tested the mechanical properties with standard laboratory equipment first. Due to the small sample size (as cast: 13 mm diameter, rotary swaged: 10 mm diameter), the degree of deformation is relatively low so that defects like pores sometimes remain in the material after casting. This leads to reduced fatigue life. To compare with commercial-sized samples, the GfE Metalle and Materialien GmbH in Nuremberg, Germany, has produced a larger ingot of Ti 6Al 4V 0.9La (diameter approx. 200 mm) and then deformed the alloy (end diameter approx. 20 mm). Recrystallisation treatment was performed in our furnaces. This is designated “industrially produced” material. All results shown for Ti6Al4V were obtained from specimens produced from standard (purchased) round bars diameter 16 mm or 20 mm.

At room temperature, the tensile strength of the lanthanum containing Ti6Al4V alloys is between 4% and 8% higher than in the standard alloy, see figure X, left. There are two causes: the grain refinement caused by the grain-boundary lanthanum particles leads to strengthened alloys, and the particles weaken the grain boundaries and cracks can propagate easier. The industrially produced material is more ductile than the material produced in laboratory conditions because the larger deformation in production leads to a recrystallised (and a more defect-free) structure. The yield tensile strength, the ultimate tensile strength and especially the minimal elongation at rupture (10.5%) of the industrially produced Ti6Al4V 0.9La material fulfil the requirements of ASTM B348 for Ti6Al4V alloys. In addition, both alloys have been investigated in fatigue tests (round tailored specimens, \( R = 0.01 \)). The Ti6Al4V 0.9La laboratory material has a fatigue limit of 480 MPa whereas the industrially processed material shows a higher fatigue limit of 550 MPa, see figure X, right. The lanthanum particles have a negative effect on the fatigue stress as they act as crack initiating points. The fatigue limit of the standard alloy Ti6Al4V here is 600 MPa which is about 10% higher compared to the lanthanum containing alloys.

Since the ductility of our REM containing alloys is a critical factor, we have used the principles outlined in this paper to design a new alloy (based on Ti6Al4V 0.9La) with increased ductility. The composition is Ti6Al2V 3Nb 0.7Fe 0.9La 0.3Si. Initial results are very promising: The maximum tensile strength of both alloys is similar but the
elongation at rupture was increased by more than 15% (from approx. 7.5% as shown in figure X, left, to minimal 9%). Our explanation is that in Ti 6Al 4V 0.9La the particles are mainly located on the grain boundaries whereas in Ti 6Al 2V 3Nb 0.7Fe 0.9La 0.3Si the particles are more homogeneously distributed.
FIG. 1: **Supplementary Movie** of a series of snapshots for deformation at 1400K. Initially we see dislocation motion changing the grain shape, grain boundary motion, and growth. At high shear, two grains remain and the mechanism changes to one involving homogeneous deformation localized in one grain. Due to periodic boundary conditions and strain control of the simulation, the two phases exchange positions.

FIG. 2: Supplementary Evolution of grain structure under shear. A slice through the sample as shear progresses, taken from five representative simulations at different temperatures. At temperatures below 1000K we see conventional deformation by dislocation motion changing grain shapes and grain boundary sliding given preferred orientation and texture. At 1200K we see significant recrystallization, followed by a transition to a nanocrystal-amorphous coexistence. At 1500K the transition occurs at lower shear, and at 53% the shear band becomes localized to a region 20 nm across. When the shearing is stopped, the shear band recrystallizes, and this nanocrystalline material is observed in TEM and X-ray experiments (Fig. 3) Representative slices through an MD sample subjected to a range of temperatures and strains. Atoms are coloured according to energy, pale blue indicating high energy environment, typically grain boundaries or amorphous regions. At low temperature and strain, it can be seen that the grain connectivity is broadly maintained, deformation being accommodated by dislocation motion. Above 1000K, the width of the boundaries begins to increase which facilitates a grain boundary sliding deformation mechanism, combined with some recrystallization. At high strain a two-phase mixture (crystalline/amorphous) is formed at 1200K. At 1500K a narrow shear band is formed with the crystalline/amorphous mixture, while the remainder of the sample remains crystalline.
FIG. 3: Supplementary Slices from the simulations imaged in Ovito. Atoms are coloured according to centrosymmetry parameter: blue bcc, green fcc, grey amorphous. The yellow lines represent atomic displacement vectors over a 100ps period, (left) 26% strain at 300K, displacement by coordinated intragranular distortion, primarily due to dislocations (centre) 22% strain at 1200K, displacement primarily within grain boundaries (right) 57% strain at 1200K, amorphization of the sample, with some residual nanocrystallites “floating” in randomly diffusing region.

FIG. 4: Supplementary Ti6Al4V without and with lanthanum. Left: Optical microscopy image of Ti6Al4V 0.9La alloy in the as-cast state, polished but unetched to clearly show the lanthanum particles mainly located on the grain boundaries. Right: Integrated intensity from Debye-Scherrer rings (transmission of bulk as-cast samples of approx. 10 mm thickness) of Ti6Al4V alloys containing 0.0, 0.9, 1.4 and 2.8% of Lanthanum. The matrix consists of α-Ti only. The particles are mainly β-La and a small volume fraction of α-La (not indexed in the figure). Tick marks for where XRD peaks from La2O3 would be are also shown: there is no evidence it, or for the presence of other Lanthanum oxides or intermetallic phases.
FIG. 5: **Supplementary.** Left: SEM image of a Ti15V 3Al 3Sn 3Cr root chip produced at $v_c = 10 \text{ m/s}$, $a_p = 0.1 \text{mm}$. The alloy is in the solution treated and water quenched state, only $\beta$-grains are present. The average grain size in the segments is $700 \mu \text{m}$. Right: The shear band consists of equiaxed, nano-crystalline $\beta$-grains. The average grain size is $15 \text{ nm}$. $\alpha$-phase has not been found. The shear band can be clearly distinguished from the segment. It is known that solution treated metastable $\beta$-Ti alloys like Ti15V 3Al 3Sn 3Cr undergo a cutting-speed dependent change in their chip-formation process from continuous (at low $v_c$) to segmented (at high $v_c$) chips. Segmented chips are more commonly obtained from aged metastable $\beta$ alloys. In contrast, alloys like Ti6Al 4V which contain mainly $\alpha$-Ti form segmented chips under almost any cutting condition, even at very low $v_c$ and low $a_p$.

FIG. 6: **Supplementary** Integrated X-ray intensity of the Debye-Scherrer rings (inset) from the synchrotron analyses of Ti15V 3Al 3Sn 3Cr and Ti15V 3Al 3Sn 3Cr 0.9La alloys in solution treated and water quenched state, $E = 85.94 \text{ keV}$, $\lambda = 0.014427 \text{ nm}$, beam size $0.25 \text{ mm} \times 0.25 \text{ mm}$. Only $\beta$-phase is present in Ti15V 3Al 3Sn 3Cr (blue line) whereas Ti15V 3Al 3Sn 3Cr 0.9La consists of $\beta$ phase and La$_5$Sn$_3$ intermetallic phase (red line). Rietveld refinement of structural parameters was unsuccessful due to the poor peak to background ratio of the REM containing phases.
FIG. 7: Supplementary (left) Schematic of the quickstop machining experiment. The sample is propelled by compressed air, and the tool is stationary. (right) The geometry of the produced sample, as used in Fig.3.

FIG. 8: Supplementary Left to right: SEM images of side and top of Ti6Al4V chips from conventional turning experiments ($v_c = 1.3\text{m/s}$) using alloys with with 0, 1.4 and 2.8 wt% of Lanthanum. Without La, shear bands are visible between segments. In the samples with La, the chip has fractured along the shear bands leading to separation of the segments, which in turn makes it impossible to make TEM images in cross section.

FIG. 9: Supplementary Mechanical properties of the standard Ti 6Al 4V alloy and the modified alloys Ti 6Al 4V 0.9La and Ti 6Al 4V 1.5La. Left: tensile properties. Right: fatigue properties of Ti 6Al 4V 0.9La alloy ($R \approx 0.01$).