Thermal shock resistance and effects of quenching on two Max Phase Bulk Materials

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Abstract.
A recently discovered material, the Max phases, has properties between metals and ceramics. In order to judge their usefulness for achieving higher temperatures in the hot zones in gas turbines, some mechanical properties have been determined at various temperatures. An earlier paper [1] deals with stress for 0.2% elongation, Young’s modulus and fracture stresses over the temperature range 22-1400 ºC.
In this paper, the Max phases were also Maxthal 211 with and without niobium addition. Thermal shock trials were made by quenching in water and by heating with various gas flames, laser beam as well as with an electric oven. Both Maxthals withstood the quenching tests and the rapid heating in electric oven, but not the laser beam and the warmer gas flames.
Keywords: Thermal shock, thermal cycling, quenching, Maxthal, Maxphases.

Introduction.
This work is part of the Mistra-financed project “Fundamental study on the use of Max phases as material in micro turbines”, carried out at KTH by the Departments of Chemical Engineering Technology (KET), Chemical Technology (KT) and Heat and Power Technology (EGI). The project main goal was to investigate the possibility to employ Maxthal, Ti2AlC (211) titanium aluminium carbide and Ti2AlC + Nb (211Nb) consisting of niobium-doped titanium aluminium carbide, two newly discovered ceramic materials in gas turbines.
Today, super alloys are usually used in high-temperature locations in gas turbines, interlaced with some sophisticated internal cooling designs. Static parts in the hottest places, e.g. guiding vanes without cooling air, would allow the turbine to run hotter with increased average engine temperature which, according to the Carnot rule, would lead to improved turbine efficiency.

Susceptibility to thermal shock of Ti3SiC2 (312) was evaluated by Barsoum and El-Raghy and published in 1996 [1]. They used small parallelepipeds (2 x 1.5 x 25 mm) which were inserted into a hot furnace and held there approximately 5-10 min at temperatures up to 1400 C and then quenched with water of ambient temperature. “The quenched surfaces were then lightly polished to remove the oxide layer that may have formed”. Then the remaining compressive strength was measured but no significant reduction in strength was observed.

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An information brochure issued by Kanthal AB, Sweden presents a table [2] where thermal shock values delta T (C) for Maxthal 312 and 211 are >1400. The source of this is said to be [1] work by Barsoum and El-Raghy.

However, the thermal shock situation when quenching by inserting a hot specimen into water is not similar to the situation in the turbine, where cold parts are subject to rapid heating by flame and/or hot gas.

Based on various tests with 211 and with 211 Nb, thermal shock-behaviour was studied. Our findings from these experiments were used for estimation of how well Maxthal could fit into turbines.

**Specimens.**

The test pieces in the quenching tests were various pieces some cm:s large and some mm:s thick, made of bulk material manufactured and supplied by Kanthal AB in Hallstahammar, Sweden. The heating tests were performed with simplified wings described below and with a similar wing of Inconel which was coated with Maxthal by plasma spraying. The wings which were subject to an electric oven heating up to 850 C and then cooling by compressed air, all withstood several thousand cycles.

The Max phases were the commercially available Maxthal 211 with a density of 4.04-4.06 and a variety with addition of 5-10 % niobium, Maxthal 211 Nb, density 4.15-4.16. The tests were performed in special devices at KTH, dept. of Chemical technology.

**Results.**

**Preliminary quench tests**

Newer the less we decided to do a simple quenching trial. In our attempt we heated up three different specimens of MAXTHAL™ one MAXTHAL™ (312) Ti₃SiC₂ (with weakened structural integrity), one MAXTHAL™ (211) Ti₂AlC and one MAXTHAL™ (211) Ti₂AlC-(Nb) to 1000°C and cooled them rapidly in water. See picture below.
The results were unambiguous, all three specimens survived the thermal shock and all three developed colored layers with the most coherent one belonging to MAXTHAL™ (211) Ti₂AlC-(Nb).

**Laser cutting test**
A 2 mm thick plate of Ti₃SiC₂ (140 x 90 mm) was submitted to a laser cutting test at the company Spånga Allmontage AB in Stockholm. This company normally deals with metal sheet, mostly steel, of different thicknesses. The result was an immediate crack of the plate in several different directions from the points where the laser beam hit. This also meant that forming by laser cutting is not possible. See picture below.

![Picture 2. Laser cutting trials on Maxthal 312. Plate is 152 x 87 mm x 2mm.](image)

**Thermal shock/Cyclic tests**
A test rig, called the temperature shock test rig, was set up. It consists of a compressed air driven, hence and forth swinging arm on which a sample of the material to be tested is mounted. The sample is a bit profile of triangular shape where two sides of the triangle are long and equal and the base side is short. This constitutes a simplified wing-profile. See below.
Picture 3. Simplified turbine-wing for thermal shock tests.
In one position of the arm the sample is hit from one side by a flame during about 2 1/2 minute and after changing position it is hit at about the same spot by a jet of compressed air for about one minute. This is repeated a desired number of times governed by a timer. See picture below.

Results with gasol-air flame.
The first sample to be tested was 211 with Niobium with a gasol-air flame. The first 60 cycles led to no visible damage to the material. Next to be tested was Inconel 792. Same results as above.

Results with acetylene- oxygen
In the second attempt acetylene and oxygen was employed instead of gasol and air, both with a pressure of ½ bar, the 211 Nb cracked instantly. Inconel 792 passed 10 cycles without remarks. However, the Inconel showed a melting mark of about 1 cm diameter, whereas the 211 Nb showed no change of the surface smoothness at all.
The cycle duration with acetylene and oxygen consisted of a 107 second long heating phase and a 50 second long cooling phase. The flame core was 2 centimeters long and 1 centimeter from the samples.

The conclusion of that trial was that the temperature of the acetylene-oxygen flame was far too intense and to concentrated for both specimens. Henrik Östling from Swerea KIMAB [3] pointed out to us that also the amount of oxygen in the acetylene flame could have played a crucial part. Namely that in our trial the heated atmosphere around the specimens was to oxygen rich while the opposite occurs in a turbine where lack of oxygen is dominating. Therefore we repeated this test with a new burner where gasol is mixed with oxygen.

Results with gasol-oxygen flame.
Here we used the same Inconel 792 profile and two similar 211 Nb profiles as we did with the former experiments in the test rig. We noticed that the gasol-oxygen flame also was able to partly melt the inconel. Since this normally doesn’t occur in a turbine, we adjusted the flame so that the inconel profile became as hot as possible without getting any melting marks.

Subsequent tests with 211 Nb-profiles showed that cracks occur nevertheless and always at the very beginning of the trial. During continued cycling no significant amount of cracks is added within a few tenth of cycles.

Consultations with prof. Torsten Strand [4] made it clear that the heating time with flames that, according to our experiments, could reach the required temperatures around 900 C, were all too short. TS recommended, based on gas turbine practice, a heating time from room temperature to 850 C of 8 minutes or from 200 C, a result of reasonable preheating, to 850 C of 6 minutes. Cooling time to 200 C should be about 2 minutes. This led us to switching the gas flames to a suitable electric oven built by our workshop. According to prof. Strand the design goal should be 6000 or at least 2000 temperature cycles.

Results electric oven.
Here we were able to adjust the oven temperature to a value (about 920 C) which made the test wing approach a temperature of the desired 850 C after a heating time of about 5 min. 45 sek. The cooling time under a stream of air was set to about 2 min.
When working with the electric oven, all temperatures could be measured with a Wahl HSA 7 F infrared thermometer. This thermometer was also checked with an adjustable electric oven (Naber, Germany) at 850 C. No difference in temperature readings were observed.
First to be tested with the electric oven was a wing of Maxthall 211. See pictures 6-8 below.
Electric oven with movable arm holding heated wing inside.

Arm holding wing immediately after switching position to air-cooling.

The situation approximately 3 seconds after the cooling has begun.

After 116 temperature cycles, no visible cracks could be seen on the wing.

Next test concerned a wing made of Maxthal 211 Nb, reaching 1998 cycles with no visible cracks.

Next a new wing of Maxthal 211 was put to test, completing 4084 cycles with no visible cracks.

**Wing of Inconel with Maxthal 211-coating by plasma spraying**

In order to combine the benefits of Maxthal with those of Inconel, a wing of the latter, size as above in picture 3, was manufactured at KTH and sent to University West in Trollhättan Sweden where it was coated with a 140 µm thick layer of plasma sprayed...
Maxthal 211-powder of size -64 +20 µm. [5] This coating method is also called High Velocity Oxy-Fuel spraying [6]
The powder was received from Kanthal. After micro-scoping at Swerea-Kimab (pictures below) it was mounted in our thermo shock device and tested by the same procedure as above, with the electric oven, reaching 6005 cycles with no visible cracks.
Before the actual tests with the coated wing begun some high resolution pictures were taken of which two are shown below.

![Picture 9. Original sprayed layer, no magnification](image1)

![Picture 10. Sprayed Ti2AlC layer, 200X](image2)

![Picture 11. Same, after 6005 cycles](image3)

The differences in pictures 10 and 11 are due to a change in topography, giving the surface material greater variations in depth and less possibilities to focus with the camera.

**Discussion**
According to the data given in [2], which compares SiC, Si3N4, Al2O3, Maxthal 312 and Maxthal 211, the most outstanding figures in favor of Maxthal are those for Thermal shock, which also is a paramount parameter for ability to use in gas-turbines. However, as described in [1], the values for thermal shock mentioned there, which are the same as in the table [2], are not calculated in the conventional way but established by experiments as already described in the introduction and only cold thermal shock.

Our own experiment with quenching confirm the ability of Maxthal to resist cold shock, but on the other hand other own experiments also show a certain sensitivity to warm shock.
How big this sensitivity is in general terms has not been possible for us to measure since our available resources have to be focused on the turbine application. That application is represented by our test stand and our simplified turbine wing and the heating and cooling methods and parameters we have chosen after discussions with mainly prof. Torsten Strand.

Calculations of the resistance to thermal shock by formulas including Youngs modulus (E), Fracture toughness (\(K\)) and thermal conductivity (\(\alpha\)), don’t give a correct answer according to Dr. Jens-Petter Palmquist of Kanthal [7] since Max-phase materials act different because deformations occur along their sliding planes. An attempt to do so just for comparison between the cold shock values in [1] and [2] and calculated values led us to one formula used by Lu and Fleck [8] for Biot numbers <1. This is calculated by the formula \(\text{Bi} = \frac{hLc/kb}{1}\) where \(h\) is the convective heat transfer coefficient which is assumed to be 100 W/m2 K, \(Lc\) is the volume of the body divided by the surface area of the body shown in picture 3, and \(kb\) is the thermal conductivity of the body \(kb\), which is 35 W/mK according to [2]. This gives \(\text{Bi} = 0.0054\).

\[\Delta T = A_4 \frac{K_c}{E\alpha\sqrt{\pi H}} 1/\text{Bi}\]

where \(A_4\) is a dimensionless number, (≈ 9.5 for cold shock and ≈ 12 for hot shock)

\(K_c\) is fracture toughness in MPam\(^{1/2}\)

\(E\) is Youngs modulus in GPa

\(\alpha\) is thermal conductivity in W/m

\(H\) is half the thickness of the material specimen

However, this formula seems to have limitations in line with the statement of Palmquist, and this is also confirmed by prof. Bo Alfredsson of KTH [9] who also clarified that the formula anyhow is not valid when \(H\) exceeds a limiting value \(H_{\text{limit}}\).

In an attempt to nevertheless use the formula on Maxthal 312, we put in values according to [6]:
\(A_3 = 9.5\), and from [2] \(K_{c}=8\) MPam\(^{1/2}\), \(a=9\times10^{-6}\) and \(\Delta T=1400\) or less.

The formula then fits for \(H=1\) m, not in accordance with the 2x1.5x25 mm parallelepipeds used in [1], and we thus assume to have exceeded the limiting value of \(H\) for Maxthal 312.

We also assume that our own experiments with Maxthal 211 and Maxthal 211Nb would have given similar results for Maxthal 312. This gives us more reason to believe that the formula used by Lu and Fleck is not applicable to the MAX-materials, and hence it wouldn’t be justified to use it in our case, which is the hot shock case.
References
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