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SPRING COLLEGE IN MATERIALS SCIENCE ON 'CERAMICS AND COMPOSITE MATERIALS'

(17 April - 26 May 1989)

FIBRE REINFORCED CERAMICS

(Continuation of Lectures)

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Tensile testing of ceramics

Specimen alignment is crucially important.

ORNL self-aligning grips. Concept is similar to that of a hydraulic clutch - load is transferred via fluid to a ring of six or eight pistons carried by each end of test-piece.

Look out for the ORNL database.

N.B. practice of "coaxing", i.e. cyclic tensile to progressively higher levels of stress.

Microstructurally, non-crystalline material at ceramic grain boundaries is usually misidentified as a glass.

In principle, it is possible to prepare a near flawless surface to a ceramic component. So, the real challenge is to avoid incorporation of internal flaws. (Incidentally, Amoco's T-1000 carbon fiber has a tensile strength of 1 msi, achieved by elimation of surface flaws by electropolishing).

JOINING CARBON-CARBON COMPOSITES

Carbon-Carbon Composite (CCC) materials maintain room temperature specific modulus to about 3000°F, maintain room temperature specific strength to above 3500°F, have a low coefficient of thermal expansion, and exhibit tolerance to impact damage.

CCC have poor resistance to oxidation

Coat with silicon carbide (SiC) for oxidation protection in 1800 to 3200°F temperature range

Below this range cracks are formed in the SiC coating due to the CTE mismatch

For oxidation protection at lower temperatures CCC is impregnated with proprietary boron compounds

Historically, CCC materials have been used as monolithic components or have been mechanically joined with metal fasteners

Some service applications for oxidation protected CCC materials used in structural components are listed in Table I.

Table I.
Applications for oxidation-protected carbon-carbon composite materials

	Space Shuttle (Nc & WLE)	Man-Rated Turbine Engines	Cruise Missile Engines	Tactial Missile Combustors	NASP (control surfaces)
Number of missions	100	Many	1	1	Many
Hot lifetime, hr	100	>2000	5	0.2	Long
Design temperature (F)	2700(a)	2500	3500	5000	>2700
Survivability temperature (F)	3000	----	----	----	>3000
Operating environment	Air	Cg	Cg	Cg	Air
Operating pressure (Atm)	<1	>1	>1	>1	<1
Strength	Low	High	High	High	High
Modulus	Low	----	----	----	High

Abbreviations: Cg --- combustion gas

Aerospace service applications which require joining CCC fall into three broad categories:

(1) Joining support structures or metal devices (test instrumentation, shafts, injectors, etc.) to hot CCC components where joints will function at temperatures of 1500 to 2200°F.

(2) Joining CCC to CCC for use on NASP and Shuttle control surfaces or in man-rated turbine engines where joints will function at temperatures of 2200 to 2700°F with short time excursions as high as 3200°F.

Finished components to be coated with an oxidation protection system such as silicon carbide.

(3) Joining CCC to CCC for use in missile motors where joints will function for short times at temperatures as high as 5000°F.

Brazing techniques that are successful with amorphous carbon, pyrolytic graphite, or polygranular graphite can be successful with CCC materials.

Joining of CCC materials has been accomplished for ambient to moderate temperature applications using modern adhesives and silver braze alloys.

CCC aircraft brakes (Concorde) which see intermittent high temperature have been repaired using nickel braze alloys which flow at 1600-2200°F.

Bonding has also been demonstrated at 4000°F using commercially available bonding systems for industrial graphite furnaces.

N.B. the carbon/graphite based industrial graphite furnace bonding systems, Dylon or C-34, have recommended design allowable shear strengths of 300 psi for service temperatures up to 4000°F.

CCC materials can be designed to have a CTE from 0.5 to 5.0 x 10^{-6} $^{o}F^{-1}$ in any direction.

Typical CTEs are 0.5 x 10^{-6} $^{o}F^{-1}$ in the X/Y plane and 3 to 4 x 10^{-6} $^{o}F^{-1}$ in the Z direction.

Graphites, carbons, none oxide ceramics, and refractory metals are often brazed for moderate to ultrahigh temperature applications

1. Graphite is not readily wetted by most conventional filler metals. Filler metals used to join graphite contain strong carbide formers since the bonding mechanism depends on carbide formation
2. Graphite has significantly lower CTEs than metals. The different volume changes on heating and cooling during joining are allowed for in the joint deisgn.
3. Liquid-solid-phase-joining (brazing) is much more successful than solid-phase-joining (diffusion welding). Fusion-joining (welding) has not been commercially successful.

Brazing materials for high temperature applications can be selected from ceramic, refractory-compound, or metallic systems.

Ceramic brazes are typically glassy oxides and are not suitable for carbon structures at elevated temperatures because of the reaction of oxygen and carbon to form carbon monoxide gas.

Refractory-compound brazes for ultrahigh temperature use are typically refractory silicides, borides, and/or carbides.

Metallic brazes can be noble metals, active metals, refractory metals, or combinations of these.

Because of the availability of carbon in CCC materials, graphites, and carbons, a eutectic braze of a metal carbide plus graphite is potentially suitable for use at ultrahigh temperatures.

Noble metal filler alloys are prepared from combinations of gold, silver, platinum, palladium, cobalt, nickel, and copper. They generally do not wet graphite, but if the graphite is pretreated with an active or refractory metal to form carbides, then these alloys may wet the graphite (carbide) surface and make way for a satisfactory joint.

Table III lists several candidate carbides.

Table III
Thermal data for active metals, refractory metals,
and their carbides

		Melting Point (°F)				
Metal	Carbide C2	Metal	Eut.1 M+C1	Carbide C2	Eut.2 C 2+G	Carbide CTE /°F
Ti	TiC	3035	3000	5550	5030	5.5
Zr	ZrC	3366	3335	6188	5270	4.4
Hf	HfC	4032	3990	7106	5760	5.5
V	VC	3450	3000	4890	4760	3.7
Nb	NbC	4474	4270	6330	5980	4.1
Ta	TaC	5425	5150	7015	6235	3.7
Cr	Cr_3C_2	3407	2790	3440	P	5.5
Mo	MoC	4730	3990	4700	4685	3.7
W	WC	6170	4910	5030	P	2.9

Abbreviations: C1 -- carbide in equilibrium with metal;
C2 -- carbide in equilibrium with graphite;
CTE -- coefficient of thermal expansion;
Eut -- eutectic;
M -- metal;
P -- peritectic

Table IV lists several commercially available filler alloys potentially applicable to brazing of surfaces pretreated with active or refractory metal to form carbides.

Table IV
Commercially available noble filler alloys that may wet pretreated graphite

Filler Metal	Temperature °F Solidus	Temperature °F Liquidus	AWS designation
Re	5756	5756	
Ru	4532	4532	
Rh	3574	3574	
Pt	3216	3216	
Pt-40Ir	3542	3614	
Pt-40Rh	3515	3542	
Pt-20Pd-5Au	2993	3083	
Pt-60Cu	2192	2282	
Pd	2826	2826	
Pd-70Ni	2354	2408	
Pd-36Ni-10Cr	2250	2300	
Pd-40Ni	2260	2260	
Pd-35Co	2246	2255	
Pd-82Cu	1976	1994	
Au	1945	1945	
Au-35Pd	2601	2624	
Au-25Pd	2516	2570	
Au-13Pd	2300	2381	
Au-34Pd-36Ni	2075	2136	
Au-25Pd-25Ni	2016	2050	
Au-65Cu	1814	1850	BAu-3
Au-62.5Cu	1814	1814	BAu-1
Au-18Ni	1742	1742	BAu-4
Ag-33Pd-3MN	2100	2250	
Ag-20Pd	1958	2120	
Ag-27Pt	1823	2120	
Ag-7.5Cu	1435	1635	BAg-19
Ni-4.5Si-3.1B	1800	1900	BNi-3
Ni-4Si-2B-1Fe	1800	1950	BNi-4
Ni-23Mn-7Si-4Cu	1800	1850	BNi-8
Cu	1980	1980	BCu-1

Potential moderate and high temperature brazes containing active and/or refractory metals are listed in Table V. These alloys have been successfully used on ceramics, graphite, or refractory metals.

Table V
Potential filler alloys containing active and refractory metals

Filler Alloy Composition	Temperature °F Solidus	Temperature °F Liquidus/ Eutectic	Source from References
Pd-Mo	2650-3200	2500-3200	24/35
Pt-55Mo	4000	3780	24/35
Pt-30W	4170	3950	24/35
Co-Cr-Si-Ni	3450		24
Mo-Ru	3450		24
Ta-Ti-Zr	3800		24
Ta-V-Nb	3300-3500(a)		25
Ta-V-Ti	3200-3350(a)		25
Ta-25Cr	3596	3596(b)	21
Ta-66Cr	3092	3092(b)	21
Ti-Zr-Nb	2912-3092(b)		26
Ti-V-Nb	3000(b)		26
Ti-V-Mo	3000(b)		26
Ti-V-Cr	2800-3000(b)		27
W-Cr	3400-6100		21
Mo-Cr	3300-4750		21
Co-Cr-Ni-Si-W	2100	2050	19 (BCo-1)
Ni-Cr-Si-Fe-B	1900	1790	19 (BNi-1)
Ni-Cr-Si-Fe-B	1970	1790	19 (BNi-1a)
Ni-Cr-Si	2075	1975	19 (BNi-5)
Ni-Cr-P	1630	1630	19 (BNi-7)
Ti-15Cu-15Ni	1760	1670	28
Ni-Cr-Si-Fe-B	2120	1780	29
Ni-W-Cr-Si-Fe-B	2000	1780	30
Co-Cr-Ni-Si-W-B	2100	2025	31
Au-Ni-Mo		1700 min.	32
Ti-48Zr-4Be	(c)	(2800)	32/33
Ti-28V-4Be	(d)	(2923)	32/33
Zr-19Nb-6Be	(e)	(3170)	32/33
Au-19/60Cr	(f)	2124	34/35
Cu-25/68Cr	(f)	1970	34/35
Cu-25/68Ti	(f)	1620 min.	34/35

(a) Liquidus temperature will vary with composition and the remelt temperature was higher when tested using Molybdenum (TZM) coupons.
(b) The remelt temperature will be raised as carbides are formed
(c) Beryllium is a strong melting point depressant used to minimize the braze temperature, if Be is eliminated the solidus becomes 2800°F
(d) As in (c), if the Be is removed the solidus becomes 2923°F
(e) As in (c), if the Be is removed the solidus becomes 3170°F
(f) Liquidus temperature will vary with composition

Braze alloys for ultrahigh temperature use can be produced by inserting a carbide-forming metal foil between the graphite pieces to be joined and heating above the metal carbide plus graphite eutectic temperature. In general, carbides are brittle and have a CTE mismatch with CCC and graphite materials.

A braze alloy composition of $60Ta-30W-10ZrH_2$ fired at 5400°F forms an adherent carbide coating on graphite. This composition has excellent thermal shock resistance and can be cycled from ambient to at least 5000°F without failure.

Increasing the graphite phase in joints using Mo, Fe, Ni, and Al results in marked increase in strength.

Samples brazed with Mo and W foils have tensile strengths above 3000 and 4000 psi, respectively, at a 4700°F

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B. BINARY TRANSITION METAL-CARBON SYSTEMS

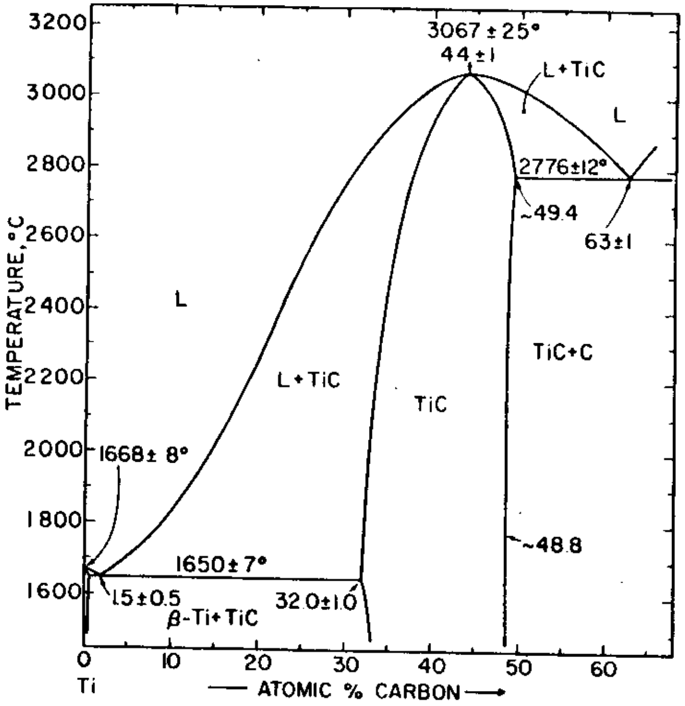


Figure III.B.1.1: Constitution Diagram of the System Ti-C.
(Temperature Error Figures Based on Estimated Overall Uncertainty)

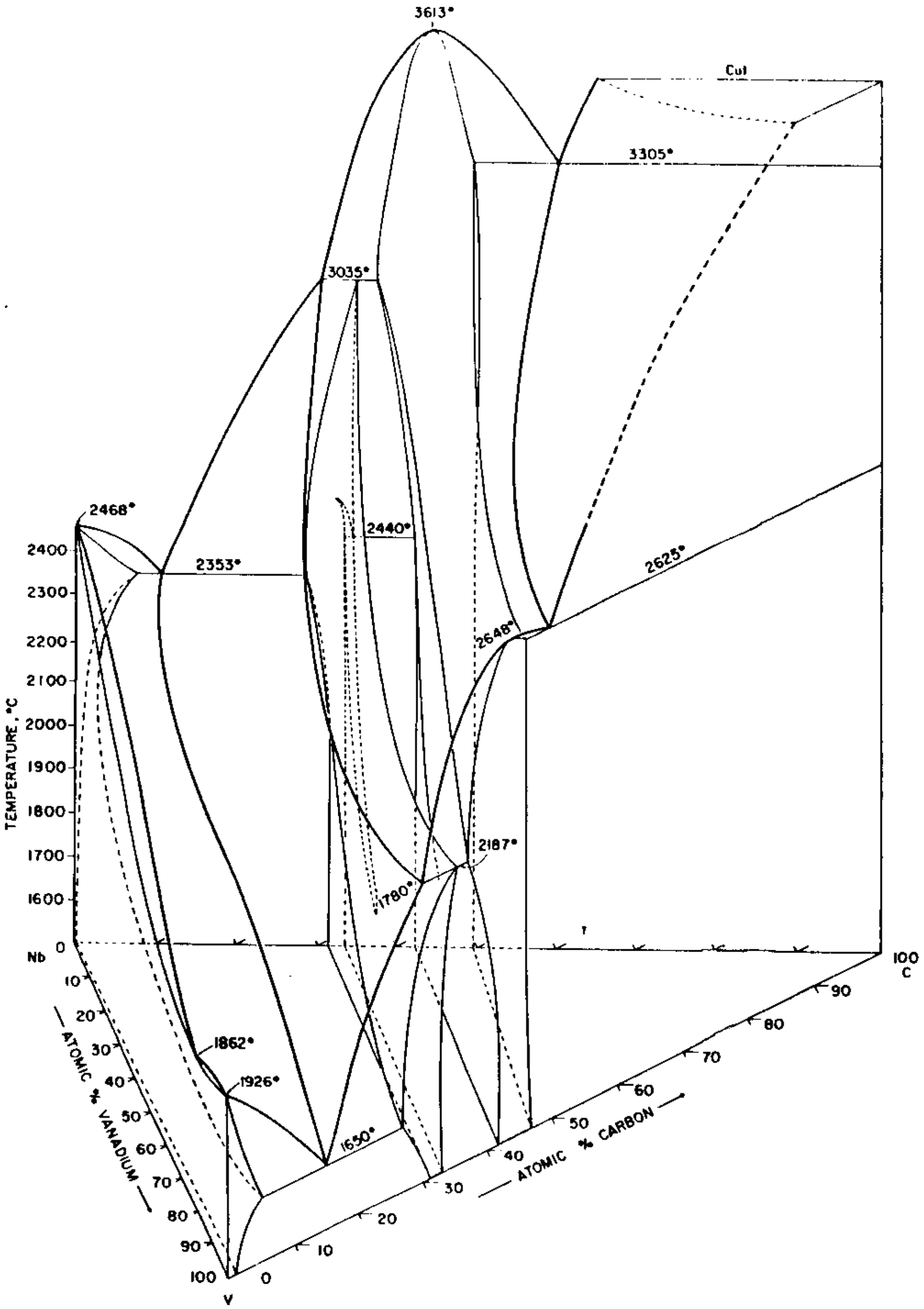


Figure III.E.10.1. Constitution Diagram of the System V-Nb-C

Tri-aluminides: potential matrix materials

Often dubbed "super" aluminum alloys because they contain 75 at% Al.

Aluminide	density (gm/cm^3)	crystal structure
Al_3Sc	3.0	$L1_2$
Al_3Ti	3.4	DO_{22}
Al_3Nb	4.5	DO_{22}
Al_3Zr	4.1	DO_{22}
Al_3V	3.7	DO_{22}

K_{Ic} ~ 2 to 3 $MNm^{-3/2}$ at room temperature (cf. SiC, K_{Ic} ~ 2 MN $m^{-3/2}$

Titanium diboride (TiB_2)

Interesting candidate matrix material because of its exceptionally high electrical conductivity (higher than Ti).

Unit cell is very stable - lattice parameter hardly varies with temperature or with impurity content.

Diamond coatings

Diamond has remarkably high thermal conductivity (20 W cm^{-2} K^{-1}), about five times higher than that of copper.

Diamond has remarkably low static coefficient of friction (~ 0.05), comparable to that of PTFE (Teflon).

Diamond is hard and abrasion resistant, an ideal coating for infra-red detectors (cadmium selenide).

Recent advance (multi-million dollar technology about to be announced by G.E.).
Conversion of thin films of graphite to diamond.
Graphite; sp^2 trigonal covalent bonds within basal plane (2D).
Diamond; sp^3 tetrahedral covalent bonds (3D).
Russian discovery - role of atomic hydrogen in puckering the (0001) surface of graphite so that the directions of covalent bonding become non-planar, approaching the morphology of the (111) surface of diamond.
400-1200°C.
CVD either thermally, plasma, or ion generated.
Thermally, use a hot tungsten wire to produce atomic hydrogen.
Present world record: 1 mm thick sheets by 1 m^2 in area.

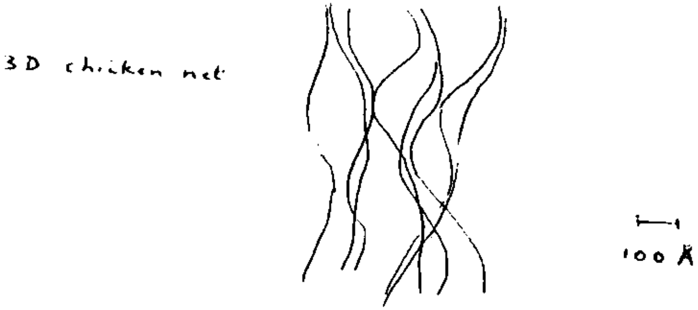
Molecular composites

Ted Hominak, WPAFB

Combine rigid rod molecules (PBT or PBO) with "coil" molecules (or other matrix material) to produce film with orthotropic properties.

Rod molecules typically 10Å long.

Rigid, and therefore readily oriented during shear flow; by shearing between counter-rotating dies, biaxial orientation can be achieved. Swollen by water uptake:



Exchange the water with matrix material, e.g. sol-gel glass (derived from an organo silicate, solution → gel, and requiring modest firing temperature, say 1,000°C for SiO_2). Phosphate glass - fuses at 6000°C.

Upshot is a composite with two multiply connected phases.

Can be blow molded or compression molded.

Axial thermal contraction of rod molecule when heated. Entropy effect.

Tensile strenth ~ 300 ksi.

Compression strength ~ 70 ksi. Buckling of rod molecules.

Anticipated applications include materials for low Earth orbit vehicles.

Atomic oxygen (single, highly energetic, oxygen ions) in low Earth orbits rapidly degrades most polymers, but not the molecular composites.