

CONF-870981--1

A REVIEW OF OXIDE, SILICON NITRIDE, AND SILICON CARBIDE BRAZING

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CONF-870981--1

ABSTRACT

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There is growing interest in using ceramics for structural applications, many of which require the fabrication of components with complicated shapes. Normal ceramic processing methods restrict the shapes into which these materials can be produced, but ceramic joining technology can be used to overcome many of these limitations, and also offers the possibility for improving the reliability of ceramic components. One method of joining ceramics is by brazing. The metallic alloys used for bonding must wet and adhere to the ceramic surfaces without excessive reaction. Alumina, partially stabilized zirconia, and silicon nitride have high ionic character to their chemical bonds and are difficult to wet. Alloys for brazing these materials must be formulated to overcome this problem. Silicon carbide, which has some metallic characteristics, reacts excessively with many alloys, and forms joints of low mechanical strength. The brazing characteristics of these three types of ceramics, and residual stresses in ceramic-to-metal joints are briefly discussed.

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In a more general sense, ceramic joining is important because of the difficulty of processing ceramic materials into large complex shapes. Joining can be used to overcome this problem and to improve reliability of ceramic components. Ceramic components initially are prepared as 'green' shapes that may be formed by cold pressing, slip casting, or injection molding, and are then densified by hot pressing, sintering, or hot isostatic pressing. Each of these processes may restrict the size and shape of the parts that can be produced, and may be relatively expensive. Therefore, the use of joining technology to produce complicated shapes provides an opportunity to overcome these primary processing difficulties.

Reliability of ceramic structures is also a major concern because of the relatively low toughness and high notch-sensitivity of ceramic materials. A crack propagating through a monolithic structure can cause catastrophic failure of the entire piece. However, joints may limit failures in large structures to a single part which can subsequently be replaced.

Ceramics cannot be joined by welding because factors such as their physical and mechanical properties, relatively low symmetry crystal structures, and disruptive phase transformations make them highly susceptible to thermal shock during cooling. However, a variety of solid-state and liquid-phase bonding techniques can be used to bond ceramics to themselves and to metals. Solid-state bonding methods typically involve hot pressing components together with or without a thin layer of a ceramic powder between the mating pieces, or direct pressureless bonding, i.e. diffusion bonding. Liquid-phase bonding techniques include brazing with either metallic alloys or glasses. The merits of these bonding approaches were recently reviewed by Nicholas and Mortimer (4).

BRAZING OF CERAMICS

In order to form ceramic braze joints for structural applications the braze filler used must satisfy the requirements of: (1) wetting and adhering to the ceramic surface, and (2) reacting with the ceramic only to the extent needed to produce a strong bond. In addition to these 'chemical' requirements, ceramic joints, especially ceramic-to-metal joints, must be able to withstand the residual stresses generated by the bonding process or by service conditions.

The difficulty of wetting and bonding to ceramic surfaces with liquid metals is related to atomic bonding in the ceramic lattice. Ceramics typically have bonds that are highly ionic or covalent in nature and electron movement through the lattice or on surfaces is restricted because the electrons are tightly bound

to the positively charged ions. In contrast, the electrons in metals are relatively free to move through the ion lattice. The difference in atomic bonding is responsible for the characteristic properties of each type of material, and the discontinuity in bonding at ceramic-metal interfaces is the cause of wetting and adherence problems. Generally, the bonding in oxides is strongly ionic and they are the most difficult of ceramics to wet (5). The bonding in borides and nitrides is less ionic, and that in carbides can be somewhat metallic in nature (5). Consequently, ceramics such as silicon nitride are expected to be less difficult to wet than oxides, and materials like silicon carbide, which display some metallic characteristics, would be somewhat better in this respect.

The following sections will discuss the brazing characteristics of three important types of structural ceramics: oxides such as alumina and partially stabilized zirconia, silicon nitride, and silicon carbide, and finally will discuss residual stresses in ceramic-to-metal joints.

Brazing Characteristics of Oxides

A considerable amount is known about the wettability and adhesion of metals on oxides (5-8). High-melting oxides like alumina and partially stabilized zirconia are typically poorly wet by pure liquid metals and many alloys. Wetting is described in terms of the contact angle θ that is established by surface energy considerations when a liquid droplet is introduced onto a solid surface. When the contact angle θ is less than 90° wetting occurs and bonding can be expected; θ greater than 90° indicates nonwetting and lack of adhesion. In general, it can be stated that the extent to which a metal will wet and adhere to an oxide surface increases with the affinity of the liquid metal for oxygen (5). The contact angles of most of the metals of commercial interest as base materials for brazing filler metals (Ag, Cu, Ni, Fe, Pd, Pt) are in the range of 120° and higher. However, metallic elements having a high affinity for oxygen such as titanium, zirconium, aluminum, lithium and others, and alloys containing these elements often form contact angles of less than 90° on oxides like alumina and therefore can be used for forming strong braze joints. Alloys containing elements such as titanium are often referred to as 'active' braze alloys.

Filler Metals for Oxide Brazing

A number of investigations (9-11) have identified alloys which will wet and bond to oxides, although most of them have not been commercially developed. Alloys of 48Ti-48Zr-4Be wt% and 49Ti-49-

Cu-2Be wt% reportedly can be used for joining oxides at brazing temperatures of 1000°C to 1050°C (9). Alloys in the Ti-V-Cr and Ti-Zr-Ta systems were found to wet and bond to alumina at temperatures near 1600°C (10). Moorhead (11) recently reported the results of an extensive investigation of the wetting behavior and bonding strength of large series of Ag-Cu-Ti, Cu-Au-Ti, Au-Ni-Ti, Cu-Au-Ni-Ti, and Ni₃Al alloys for brazing alumina.

A limited number of braze filler metals are now available for brazing oxides. These active braze alloys include Cusil-ABA (a Ag-Cu eutectic alloy containing Ti), and Incusil-15 ABA and Incusil-10 ABA (alloys of Ag-Cu-In-Ti) which are products of GTE Wesgo, and the Lucanex alloys (Ag-Cu-In-Ti and Ag-Cu-Ni-Ti alloys) which are available through Handy & Harmon. No braze filler metals are currently commercially available for brazing at temperatures above about 900°C.

Brazing Characteristics of Silicon Nitride

No detailed studies of the wetting behavior of silicon nitride were known to the authors at the time of this writing. However, there is some indication that Si₃N₄ behaves similarly to oxides such as alumina in that it is wet poorly or not at all by pure metals and precious metal alloy braze filler metals (12,13).

Filler Metals for Silicon Nitride

Those commercially available active braze alloys that will bond oxides reportedly are also useful for brazing Si₃N₄. Also, amorphous alloys of CuTi and NiTi₃ are reported to produce strong braze joints of silicon nitride (14). It has also been demonstrated that Si₃N₄ can be joined with standard commercially available braze filler metals by vapor coating the ceramic surfaces with titanium prior to brazing (13). This technique was used to make braze joints of Si₃N₄ at temperatures up to 1130°C, well beyond the limits imposed by the Ag-Cu-based active braze alloys.

Brazing Characteristics of Silicon Carbide

A considerable amount is known about the wetting characteristics of silicon carbide single crystals (15). Pure indium, tin, silver, and gold reportedly do not wet silicon carbide. Copper apparently does not wet silicon carbide under what would be considered normal brazing conditions, but will react and spread over the surface after holding for relatively long times at high

temperatures. Manganese, iron, cobalt, and nickel reportedly wet silicon carbide crystals.

Experiments in our own laboratory have confirmed that pure nickel and nickel-based brazing alloys will wet sintered silicon carbide. However, these liquid metals generally react so vigorously with silicon carbide as to be corrosive. The problems associated with brazing silicon carbide with nickel alloys are illustrated in Fig. 1, which shows a cross sectional view of the microstructure under a nickel droplet that was melted on silicon carbide under vacuum in a sessile drop experiment. The liquid nickel wetted the silicon carbide very well but upon cooling the solidified nugget detached from the ceramic substrate because of the large mismatch in thermal expansion coefficient between silicon carbide and nickel. A very thick reaction zone comprised of brittle carbides and Ni-Si intermetallic phases was produced under the droplet. Small secondary cracks are also visible in the silicon carbide. In this particular experiment the temperature was set just above the melting point of nickel and the specimen was held there only long enough to ensure that the nickel was completely melted. Clearly, controlling the extent of reaction on silicon carbide will be a major concern in developing brazing methods and filler metals for high temperature applications.

Filler Metals for Silicon Carbide

There are no commercially available brazing filler metals made specifically for joining silicon carbide. However, several studies of silicon carbide brazing have been made. In one investigation pure germanium metal and a 50 wt.% Ge-Si solid solution were used to braze reaction bonded silicon carbide (16). It was reported that the joints showed a positive dependence of flexure strength with temperature, and that joints tested at 1050°C had strengths near 400 MPa. Amorphous alloys with compositions of CuTi and NiTi₃ (14), as well as TiSi₂ (17) powder have also been used for brazing silicon carbide. Work in our laboratory has indicated that silicides of chromium, molybdenum, and zirconium will wet and bond silicon carbide, but that strong joints cannot be obtained because of incipient cracking as the liquid alloy solidifies. Figure 2 (a) shows a cross sectional view of a solidified droplet of CrSi₂ on silicon carbide. Excellent wetting was obtained and extensive reaction with the substrate was avoided, but the CrSi₂ was severely cracked. Figure 2 (b) shows a cross sectional view of a silicon carbide joint brazed with CrSi₂. Again, a large number of cracks developed in the CrSi₂ during cooling. The susceptibility of the silicides to cracking is apparently caused by their low symmetry crystal structures and low grain boundary strengths.

Residual Stresses in Ceramic/Metal Joints

The physical property data presented in Table 1 shows that structural ceramic generally have much lower thermal expansion coefficients than metallic alloys. Even small differences in thermal expansion characteristics can generate large residual stresses in ceramic-to-metal joints (13), and because of the brittle nature of ceramics low strength joints or complete mechanical failure upon cooling from the brazing temperature can occur (13).

One solution to this problem is the introduction of transition materials between the ceramic and metal components that can isolate the ceramic from stresses due to mismatches in thermal expansion behavior. This technique was successfully used for brazing 112 mm partially stabilized zirconia disks to nodular cast iron components representing diesel engine piston heads (18). The success of this approach was attributed to using titanium metal as a transition piece between the oxide and the cast iron. The titanium has excellent ductility, and a thermal expansion coefficient that closely matches that of zirconia. Because of these properties the titanium could accommodate enough of the mismatch strain to prevent cracking of the ceramic after the joint was formed.

Because of the relatively high elastic moduli and very low thermal expansion coefficients of silicon carbide and silicon nitride joining these ceramics to metals represents an even bigger challenge than for the oxide ceramics. Table 1 shows that only some of the refractory metals, and high melting temperature precious metals approach the thermal expansion coefficient of these ceramics (3 to 5 $\mu\text{in./in./}^\circ\text{C}$). Consequently, there is a limited list of candidates for use as transitional pieces for accommodating strains due to thermal expansion mismatch. Furthermore, some of the best candidates in terms of thermal expansion characteristics are not practical. Tungsten appears to be a likely choice for forming transitional pieces for either silicon carbide or silicon nitride, but its low ductility is a disadvantage and its poor oxidation resistance would preclude its use in temperature structural joints. Other refractory metals suffer from similar problems in addition to high material cost. Perhaps the most viable means of joining silicon carbide and silicon nitride would rely on transitional pieces of graded constitution as has been used with success for joining graphite to structural alloys (19).

ACKNOWLEDGEMENT

The authors would like to thank ___ and ___ for reviewing the manuscript. This work was sponsored by the U. S. Department of Energy, Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Systems, as part of the Ceramic Technology for Advanced Heat Engines Project of the Advanced Materials Development Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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FIGURE 1. MICROSTURCTURE AT INTERFACE BETWEEN NICKEL DROPLET AND SILICON CARBIDE

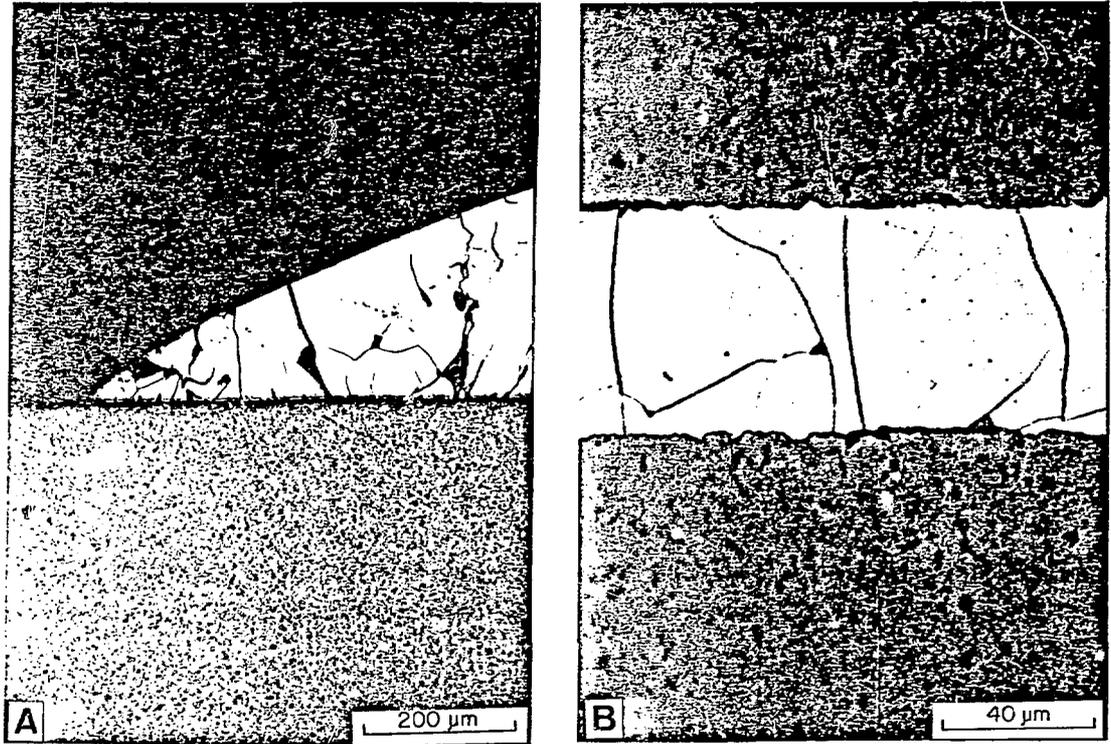


FIGURE 2. CROSS SECTIONAL VIEWS OF (A) CrSi_2 MELTED ON SILICON CARBIDE, AND (B) SILICON CARBIDE JOINT BRAZED WITH CrSi_2 .

Properties of Ceramics^a

Material	Crystal structure	Theoretical density (Mg/m ³)	Knoop or Vickers hardness (GPa)	Transverse rupture strength (MPa)	Fracture toughness (KJ/Cm ^{3/2}) (MPa·m ^{1/2})	Young's modulus (GPa)	Poisson's ratio	Thermal expansion (×10 ⁻⁶ K ⁻¹)	Thermal conductivity [W/(m·K)]	Specific heat [J(Kg·K)]	Emissance ^b	Thermal shock resistance parameter ^c
Glass ceramics	Variable	2.4-5.9	6-7	70-350	2.4	83-138	0.24	5-17	2.0-5.4 at 400 K 2.7-3.0 at 1200 K	795-1298	0.9 at 300 K (T)	1.2 ^d
Pyrex glass	Amorphous	2.52	5	69	0.75	70	0.2	4.6	1.3 at 400 K 1.7 at 800 K	335 at 100 K 1170 at 700 K	0.85 at 100 K (N) 0.85 at 900 K (N) 0.75 at 1100 K (N)	0.2
TiO ₂	Rutile tetragonal Anatase tetragonal Brookite orthorhombic	4.25 3.84 4.17	7-11	69-103	2.5	283	0.28	9.4	8.8 at 400 K 3.3 at 1400 K	799 at 400 K 920 at 1700 K	0.83 at 450 K (T) 0.89 at 1300 K (T)	0.2
Al ₂ O ₃	Hexagonal	3.97	18-23	276-1034	2.7-4.2	380	0.26	7.2-8.6	27.2 at 400 K 5.8 at 1400 K	1088	0.75 at 100 K (N) 0.53 at 1000 K (N) 0.41 at 1600 K (N)	6.5
Cr ₂ O ₃	Hexagonal	5.21	29	>262	3.9	>103		7.5	10-33 at 350 K	670 at 300 K 837 at 1000 K 879 at 1600 K	0.69 (N) 0.91 (N)	2.7
Mullite	Orthorhombic	2.8		185	2.2	145	0.25	5.7	5.2 at 400 K 3.3 at 1400 K	1046	0.5 at 1200 K (N) 0.65 at 1550 K (N)	0.9
Partially stabilized ZrO ₂	Cubic, monoclinic, tetragonal	5.70-5.75	10-11	600-700	8-9 at 293 K 6-6.5 at 723 K 5 at 1073 K	205	0.23	8.9-10.6	1.8-2.2	400		0.5
Fully stabilized ZrO ₂	Cubic	5.56-6.1	10-15	245	2.8	97-207	0.23-0.32	13.5	1.7 at 400 K 1.9 at 1600 K	502 at 400 K 669 at 2400 K	0.82 at 0 K (N) 0.4 at 1200 K (N) 0.5 at 2700 K (N)	0.8
Plasma-sprayed ZrO ₂	Cubic, monoclinic, tetragonal	5.6-5.7		6-80	1.3-3.2	48 21 at 1373 K 172	0.25	7.6-10.5	0.69-2.4		0.61-0.68 at 700 K (T) 0.25-0.4 at 2800 K (T)	0.2
CeO ₂	Cubic	7.28					0.27-0.31	13	9.6 at 400 K 1.2 at 1400 K	370 at 300 K 520 at 1200 K	0.65 at 1300 K (T) 0.45 at 1550 K (T) 0.40 at 1800 K (T)	
TiB ₂	Hexagonal	4.5-4.54	15-45	700-1000	6-8	514-574	0.09-0.13	8.1	65-120 at 300 K 33-80 at 1100 K 54-72 at 2300 K	672 at 300 K 1155 at 1400 K	0.8 at 1000 K (N) 0.85 at 1400 K (N) 0.4 at 2800 K (N)	21
TiC	Cubic	4.92	28-35	241-276		430	0.19	7.4-8.6	33 at 400 K 43 at 1400 K	544 at 293 K 1046 at 1366 K	0.5 at 800 K (N) 0.65 at 1500 K (N) 0.38 at 2800 K (N)	2.2
TaC	Cubic	14.4-14.5	16-24	97-290			0.24	6.7	32 at 400 K 40 at 1400 K	167 at 273 K 293 at 1366 K	0.2 at 1600 K (N) 0.33 at 3000 K (N)	3.7
Cr ₃ C ₂	Orthorhombic	6.70	10-18	49		373		9.8	19	502 at 273 K 837 at 811 K 197-544		0.2
Cemented carbides	Variable	5.8-15.2	8-20	758-3275	5-18	396-654	0.2-0.29	4.0-8.3	16.3-119			13 ^e
SiC	α hexagonal β cubic	3.21 3.21	20-30	Sintered 96-520 at 300 K 250 at 1273 K Hot pressed 230-825 at 300 K 398-743 at 1273 K 1034-1380 at 300 K 2060-2400 at 1473 K	Sintered 4.8 at 300 K 2.6-5.0 at 1273 K Hot pressed 4.8-6.1 at 300 K 4.1-5.0 at 1273 K 5-7	207-483	0.19	4.3-5.6	63-155 at 400 K 21-33 at 1400 K	628-1046	0.85 at 400 K (N) 0.80 at 1800 K (N)	31
SiC (CVD)	β cubic	3.21	28-44			415-441		5.5	121 at 400 K 34.6 at 1600 K	837 at 400 K 1464 at 2000 K		
Si ₃ N ₄	α hexagonal β hexagonal	3.18 3.19	8-19	Sintered 414-650 Hot pressed 700-1000 Reaction bonded 250-345	Sintered 5.3 Hot pressed 4.1-6.0 Reaction bonded 3.6	304	0.24	3.0	9-30 at 400 K	400-1600	0.9 at 600 K (N) 0.8 at 1300 K (N)	16
TiN	Cubic	5.43-5.44	16-20			251		8.0	24 at 400 K 67.8 at 1773 K 56.9 at 2573 K	628 at 273 K 1046 at 1366 K	0.4 at 800 K (N) 0.8 at 1400 K (N) 0.5 at 2100 K (N) 0.33 at 3000 K (N)	
Graphites (with grain)	Hexagonal	2.21	35-85 ^f	0.46-207	0.5-1.8	1.4-34.5	0.07-0.22	0.1-19.4	1.67-518.8	711-1423	0.8 at 1366 K (T)	135
Cast irons	Cubic	5.5-7.8	1-7	50-1186	37-45	83-211	0.17	8.1-19.3	46-52	460		32 ^g

^aPublished in: W. J. Lackey, D. P. Stinton, G. A. Cerny, L. L. Fehrenbacher, and A. C. Schaffhauser, "Ceramic Coatings for Heat Engine Materials - Status and Future Needs," *Proceedings of International Symposium on Ceramic Components for Heat Engines, October 17-21, 1983, Hakone, Japan.*

For data references see: W. J. Lackey, D. P. Stinton, G. A. Cerny, L. L. Fehrenbacher, and A. C. Schaffhauser, *Ceramic Coatings for Heat Engine Materials - Status and Future Needs*, ORNL/TM-8959, Oak Ridge National Laboratory, Oak Ridge, Tennessee.

^bN, normal; T, total hemispherical.

^cCalculated using $R = ka(1-\mu)/Ea$.

^dCorning grade 9606.

^eKennametal grade K-701.

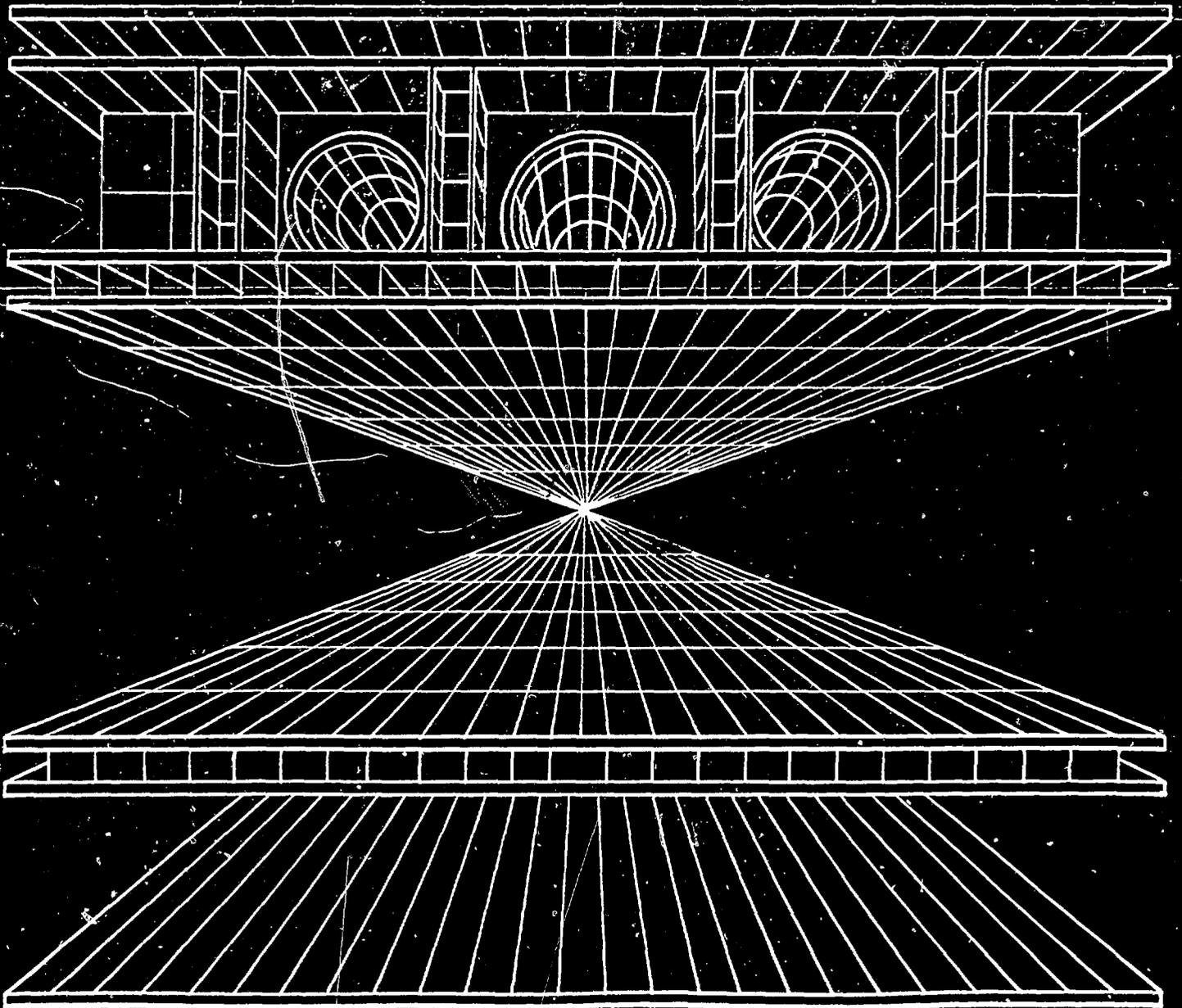
^fScletroscope.

^gGray cast iron.

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