A STUDY OF METAL IGNITIONS

I. THE SPONTANEOUS IGNITION OF TITANIUM*

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SUMMARY

Spontaneous ignition of massive shapes of titanium can occur at room temperature when a fresh, oxide-free metal surface is exposed to oxygen under pressure. Such a surface can be produced by the rupture of a titanium specimen under tension. If these surfaces are exposed to oxygen pressure in excess of 350 p.s.i.g. spontaneous ignition of the sample occurs. With dilute oxygen, using helium or steam as a diluent, higher pressures are required for ignition.

Spontaneous ignition at various concentrations of oxygen was investigated and the effect of temperature on ignition limits was also determined. The hypothesis is suggested that only those metals whose oxides are soluble in the metal will ignite spontaneously and ignition will occur only if the initial reaction is vigorous enough to raise the surface temperature to the melting point of the metal or an eutectic.

INTRODUCTION

Spontaneous ignition of massive titanium was investigated because of concern over inexplicable failures of titanium parts used in test loops in the Homogeneous Reactor Program at Oak Ridge[1,2]. The damage had the appearance of a burn, and metallographic examination suggested that the α-β transformation temperature (850°C) had been exceeded. The presence of titanium oxide further substantiated the suspicion that the failures were due to a spontaneous ignition of the metal in contact with either hot aqueous solutions or the atmosphere above it, consisting mostly of oxygen under pressure.

Since these reactions occurred spontaneously and appeared to be self-sustaining, they constituted a considerable potential hazard. A project was therefore initiated at Stanford Research Institute to answer the following questions: (1) How are such processes initiated and (2) once initiated, how are they sustained?

SPONTANEOUS IGNITION OF TITANIUM BARS AND ITS LIMITS

Equipment

Suspecting that ignitions occurred when the protective oxide film normally covering the surface of titanium is disturbed, an apparatus was designed which would make possible exposure of oxide-free surfaces to various environments.

A stainless steel high pressure vessel was equipped with a sliding bar, which was in

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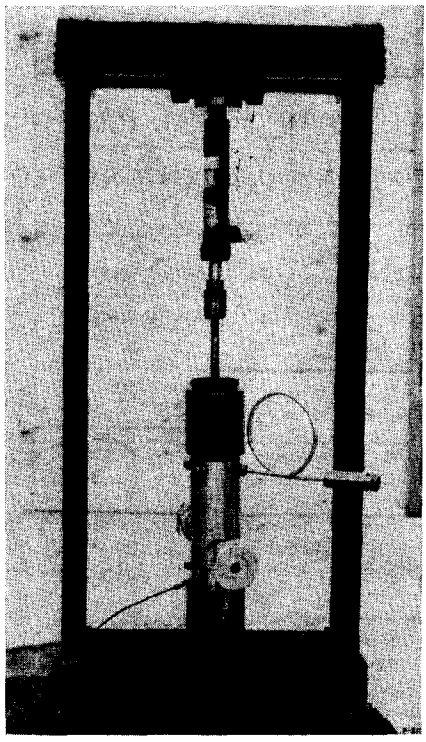

Fig. 1. Reactor assembly.

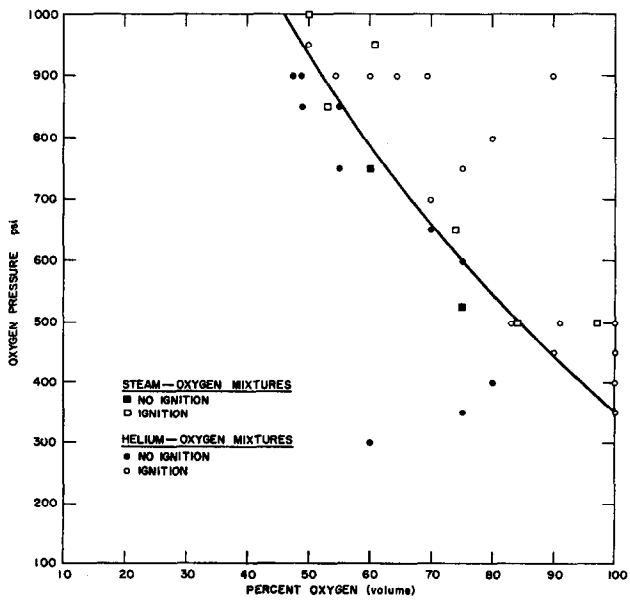

Fig. 2. Reactions of titanium with helium–oxygen and steam–oxygen mixtures. Static tests.

turn connected to a hydraulic ram. Titanium bars, fabricated in the shape of a tensile test specimen, were connected to the sliding bar and broken in tension, thus exposing a fresh surface to the atmosphere. The composition and pressure of the atmosphere surrounding the sample could be varied over wide limits. This equipment is shown in Fig. 1.

Static tests

The procedure used consisted of placing a sample in the reactor, securing the reactor in the steel frame located in an explosion test pit, and pressurizing to the desired pressures. When proper conditions were attained, the sample was broken in tension by the hydraulic pull-ram. The occurrence of an ignition reaction was indicated by a sudden decrease of the gas pressure. The reactor was then vented and opened up for visual inspection of the contents.

The lower ignition limits were established by breaking a series of titanium rods. The pressure for a given oxygen and diluent composition was increased from run to run, until ignition occurred. Sometimes "initial" ignition was noted: that is, the test sample would show burned spots, usually on the edges of the fresh surface, but the ignition did not propagate. The "initial" ignition results were observed under conditions close to the borderline shown in Fig. 2. The results of tests with helium–oxygen mixtures are shown in Table I. Table II shows results obtained under otherwise similar conditions, but using 1/2-in. strips of 12-mil titanium foil in place of the 1/4-in. rod. A third set of results is shown in Table III, where steam was used as a diluent in place of helium.

All of these data are shown graphically in Fig. 2. The line drawn through these points indicates the boundary between the go and no-go regions. There seems to be no significant difference between the behavior of titanium foil and rod, nor between helium and steam as a diluent.

Most of the samples of titanium used in the static experiments consisted of 5-in. lengths of 1/4-in.-diameter rod, reduced to a 1/8-in.-diameter cross section near the middle, with a 1/2-in. taper. Several runs were made with differently shaped specimens. Some rods were reduced to 1/8 and 1/16 in., respectively, by a square-cut groove

TABLE I

REACTIONS OF 1/4-in. TITANIUM ROD WITH HELIUM–OXYGEN MIXTURES

(Static conditions)

P_{O_2} (p.s.i.g.)	P_{He} (p.s.i.g.)	P_{total} (p.s.i.g.)	O_2 (%)	Ignition
300	200	500	60	no
400	100	500	80	no
300	100	400	75	no
400	—	400	100	yes
500	100	600	83	initial
500	50	550	91	initial
900	100	1000	90	yes
800	200	1000	80	yes
700	300	1000	70	initial
750	250	1000	75	(1/2 only)
950	950	1900	50	yes
900	1000	1900	47.5	no

TABLE II

REACTIONS OF 0.012-in. TITANIUM FOIL WITH HELIUM–OXYGEN MIXTURES

P_{O_2} (p.s.i.g.)	P_{He} (p.s.i.g.)	P_{total} (p.s.i.g.)	O_2 (%)	Ignition
500	—	500	100	yes
450	—	450	100	yes
350	—	350	100	no
350	—	350	100	yes
900	950	1850	48.5	no
900	750	1650	54.5	yes
900	600	1500	60.0	yes
900	400	1300	69.0	yes
900	500	1400	64.0	yes
700	300	1000	70	yes
450	50	500	90	yes
850	900	1750	48.5	no
850	700	1550	55.0	no
650	280	930	70	no
600	200	800	75	no
500	100	600	83.5	no

TABLE III

IGNITION IN PRESENCE OF STEAM

P_{O_2} (p.s.i.g.)	P_{steam} (p.s.i.g.)	P_{total} (p.s.i.g.)	O_2 (%)	Temperature (°C)	Ignition
500	15	515	97	100	initial
500	100	600	83	165	initial
650	225	875	74	200	initial
950	600	1550	61	250	yes
1000	1000	2000	50	285	yes
525	175	700	75	188	no
750	500	1250	60	241	no
850	750	1600	53	275	yes

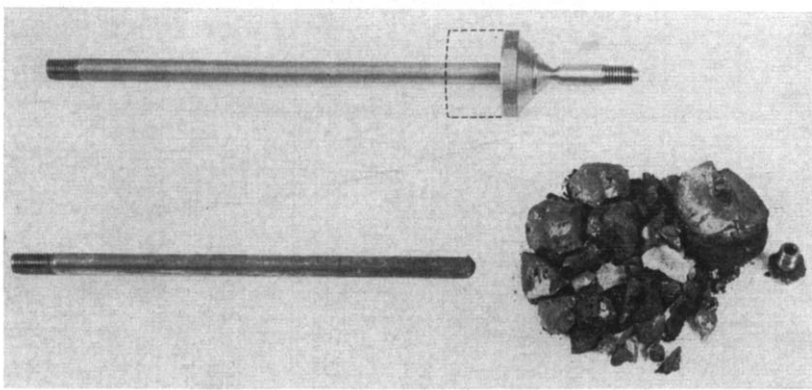

Fig. 3. Ignition of titanium poppet.

near the center, resulting in a very abrupt change in diameter. Another sample was machined from 1-in. round stock to resemble the poppet in the valves mentioned in

ORNL Report No. 56-8-214. Its cylindrical section was about 1 in. long, with a 60° taper coming to a 1/8-in. point attached to a 1/4-in. rod. (See Fig. 3: the burned sample had a longer cylindrical section.) This sample weighed 72 g. In still other runs, 1/2-in. strips of 0.012-in. titanium foil were used. All of these samples ignited readily upon breaking and were completely consumed or melted, even though in the case of the large poppet only 25% of the amount of oxygen required for complete oxidation was present. These tests indicate that, in the presence of oxygen at the necessary pressures, exposure of a very small fresh area can result in a self-sustaining reaction.

Several different titanium alloys were used, such as A-55, A-110 AT, and 6 Al-4V. The results obtained with these samples did not differ within the limits of experimental error, which are of the order of ± 25 p.s.i.g.

The above experiments were carried out at room temperature. The effect of elevated temperature on ignition conditions was also examined. The pressure vessel

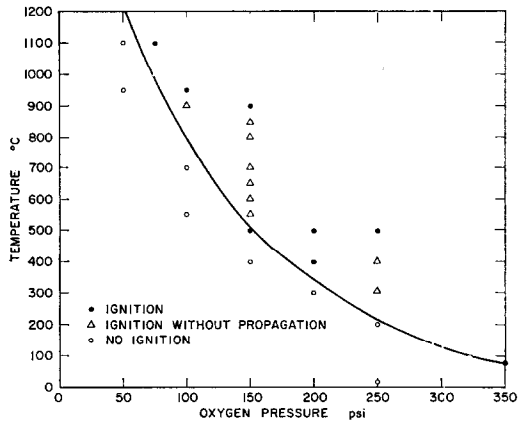

Fig. 4. Effect of initial temperature on ignition of titanium rods.

was modified by insulating the pull-ram electrically from the body of the bomb. This was done by enlarging the guide hole of the rod connecting the pull-ram and the sample, filling it with a reinforced Epoxy resin and redrilling to size. With this insulating sleeve between the extension rod and the body of the bomb, a heavy AC current could be passed through the mounted sample. The temperature of the narrowest portion of the sample as a function of the applied voltage was determined with an embedded platinum, platinum–10% rhodium thermocouple.

In the actual runs the temperature was not measured, but was estimated from the applied voltage. This procedure resulted in an uncertainty of about ± 5% in the temperature assumed. The sample was heated in the presence of oxygen until it reached the desired temperature (10 min). The current was then shut off and the sample was broken in tension. The results are tabulated in Table IV and shown in Fig. 4. The minimum oxygen pressure for spontaneous ignition upon rupture of the sample drops from 350 p.s.i.g. at room temperature to 210 p.s.i.g. at 300°C, to 150 p.s.i.g. at 500°C, and to 75 p.s.i.g. at 1000°C. The wide range of "ignition but no propagation" indicated in Table IV seems to contradict our previous experience,

TABLE IV

TEMPERATURE DEPENDENCE OF IGNITION TEMPERATURE OF TITANIUM

P_{O_2} (p.s.i.g.)	Temperature (°C)	Ignition
250	500	Yes
250	400	Yes
250	300	Yes
250	300	Yes
250	200	No
250	room	No
200	500	Yes
200	400	Yes
200	300	No
150	m.p.	Yes
150	900	Yes
150	850	Yes
150	800	Yes
150	700	Yes
150	650	Yes
150	600	Yes
150	550	Yes
150	500	Yes
150	500	Yes
150	400	No
100	950	Yes
100	900	Yes
100	700	No
100	500	No
75	1100	Yes
50	1100	No
50	950	No

which indicated that propagation occurred readily once the sample was ignited. This situation is, however, probably due only to a peculiarity of our experimental arrangement: since the sample was heated by passing a current through it, only the narrowest portion was at the predetermined temperature. The steep temperature gradient from the narrow section to the end of the rod may have resulted in effective quenching of the ignition. This view is supported by the fact that propagation of the ignited sample did occur more regularly when a sample with a longer conical section was used.

To gain a more detailed understanding of the reaction taking place at the freshly formed titanium surface, the reaction was recorded by a Fastax camera, at a framing rate of about 6000 frames per second. The burning of the rod provided sufficient illumination to expose the film. Synchronization was achieved by prestressing the sample to the point where the next stroke of the hydraulic pump would cause rupture. The camera was started, and the sample was broken 0.2–0.4 sec later. This procedure allowed the camera to come up to speed and left 0.3–0.5 sec for recording the ignition.

Selected frames are shown in Figs. 5 and 6. The first frame of Fig. 5 clearly shows the flash which enveloped the fresh surface an instant after the rupture. A puff of

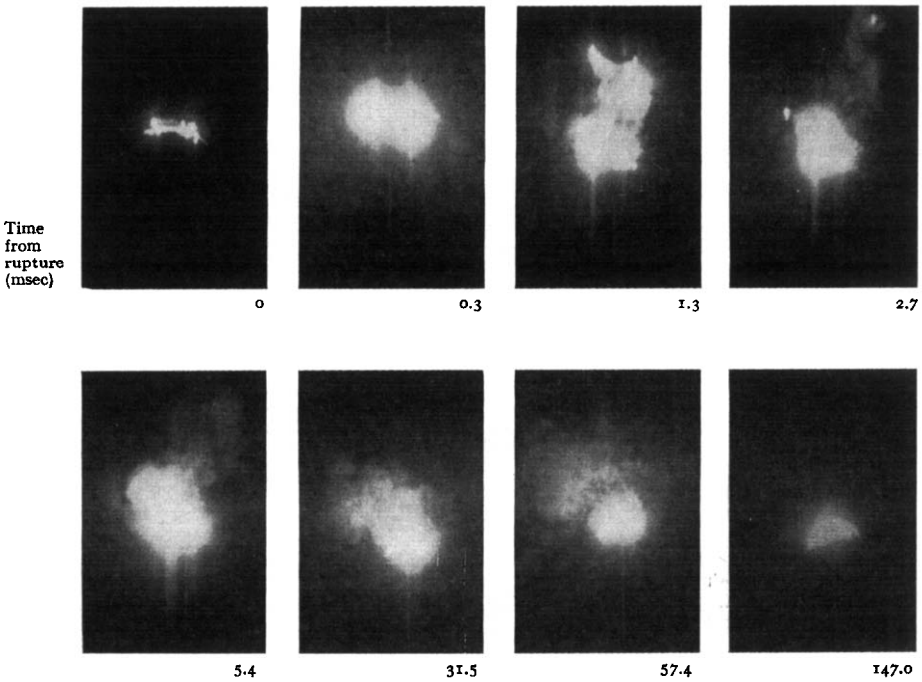

Fig. 5. Ignition of titanium rod.

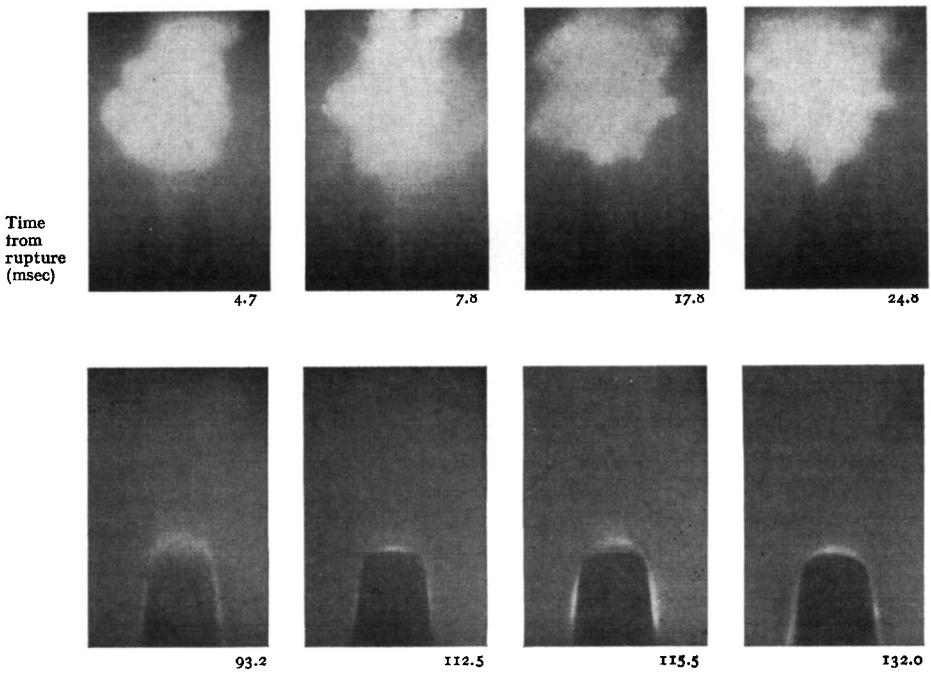

Fig. 6. Ignition of titanium rod.

white smoke appears and the rod begins to burn rather quietly, without much sparking, melting down as time goes on (see last three frames of Fig. 6).

IGNITION LIMITS OF TITANIUM SHEET UNDER DYNAMIC CONDITIONS

The reactor was equipped with a special head to hold down a titanium rupture disk, which was broken by a spring-loaded plunger. Either water or steam could be selected as the material initially in contact with the disk, depending upon the orientation of the reactor. A very high degree of turbulence existed as the contents of the reactor were discharged through the break in the rupture disk. The thickness of the disks varied from 4 to 12 mils. Fig. 7 shows the arrangement with the rupture disk facing downward.

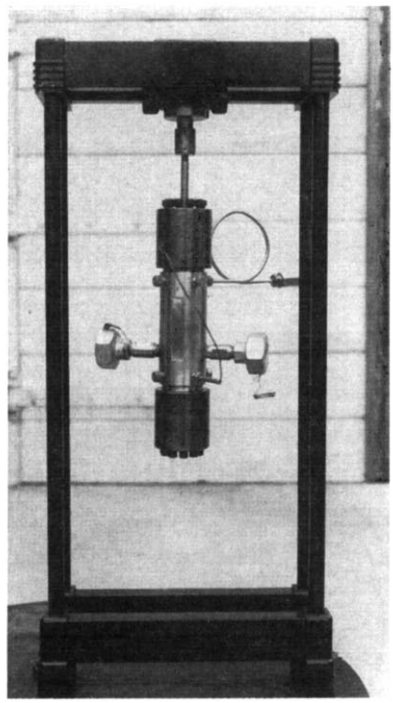

Fig. 7. Reactor assembly for use with rupture disk.

The relationship between oxygen pressure and concentration necessary to produce autoignition of a titanium specimen under dynamic conditions of gas flow was determined in a series of runs in which the oxygen concentration at a given total pressure of oxygen and diluent was increased until ignition occurred. The results, given in Fig. 8 and Table V, show that ignition occurs much more readily under dynamic than under static conditions: pure oxygen at 50 p.s.i.g. pressure, streaming past a fresh surface, produced autoignition. The ignition limits are much lower throughout the whole range of oxygen concentrations. Fig. 9 shows the appearance of a reacted disk.

A number of runs were made with the rupture disks facing down, so that the disk

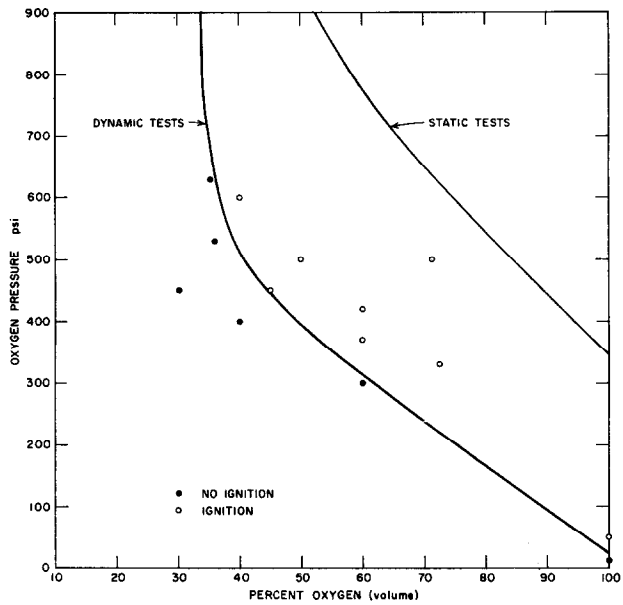

Fig. 8. Reactions of titanium with helium–oxygen mixtures. Dynamic tests.

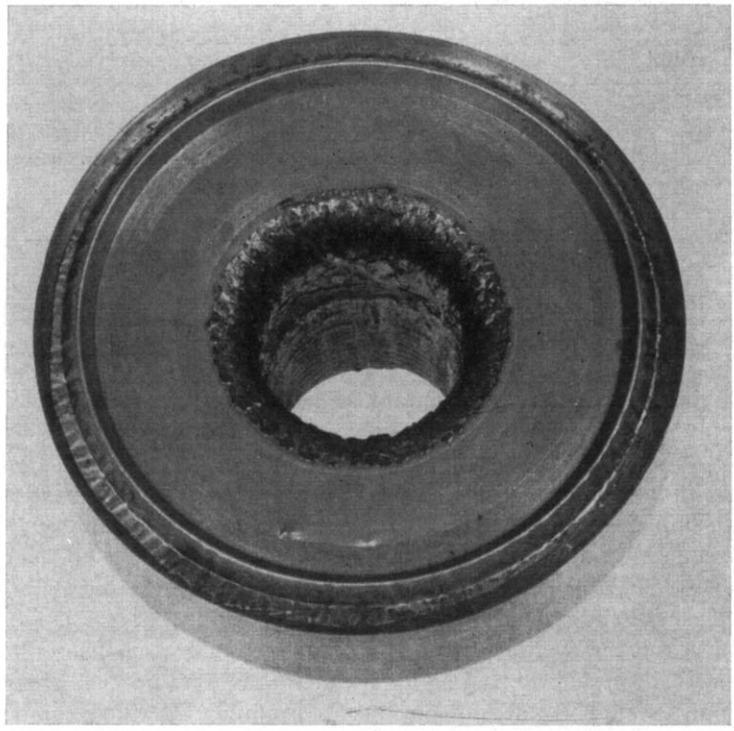

Fig. 9. Rupture disk after reaction.

TABLE V

REACTIONS OF TITANIUM WITH HELIUM–OXYGEN MIXTURES UNDER DYNAMIC CONDITIONS

Foil thickness (in.)	P_{O_2} *(p.s.i.g.)*	P_{He} *(p.s.i.g.)*	P_{total} *(p.s.i.g.)*	O_2 *(%)*	*Ignition*
0.003	350	—	350	100	yes
0.003	300	—	300	100	yes
0.003	250	—	250	100	yes
0.003	200	—	200	100	yes
0.003	150	—	150	100	yes
0.003	100	—	100	100	yes
0.003	50	—	50	100	yes
0.003	10	—	10	100	no
0.012	50	—	50	100	yes
0.008	500	500	1000	50	yes
0.008	400	600	1000	40	no
0.008	450	550	1000	45	yes
0.008	420	280	700	60	yes
0.008	370	250	620	60	yes
0.008	340	130	470	72.5	yes
0.008	300	200	500	60	no
0.012	450	1050	1500	30	no
0.012	450	1050	1500	30	no
0.012	540	960	1500	36	no
0.012	600	900	1500	40	yes
0.012	630	1170	1800	35	no
0.012	500	200	700	71.5	yes

was originally in contact with oxygenated water. The concentration of oxygen in water was varied by increasing the oxygen pressure above the water up to 1850 p.s.i.g., which resulted in concentrations up to 7200 p.p.m. dissolved oxygen. In no case was there any indication of reaction of the oxygenated water with titanium even under streaming conditions.

PROPAGATION STUDIES

To start a self-sustaining reaction between titanium and oxygen, a very rapid rate of reaction has to be attained to raise the temperature of the specimen enough to continue the burning. If the initial energy is supplied from exterior sources, milder conditions should be adequate to maintain the reaction.

A different reactor was built for these experiments. It consisted of a cylindrical body 4 in. in diameter and 8 in. long, with a standard head and closure. Two insulated lead-ins were provided in the head. The sample was fastened to these leads. Power for heating the sample was furnished by an a.c. welding transformer capable of delivering 175 amp at 20 V. A 1/4-in. high pressure line and a valve completed the setup. The samples consisted of 1/2-in. strips of titanium foil 0.012 in. thick and about 6 in. long, bent into a U shape and notched at one end.

For the first run the reactor was filled with oxygen at 1 atmosphere pressure and the reaction was initiated by passing a current through the notched sample until it melted (about 5 sec). The reaction continued, consuming the whole sample. Air was used in another run; under these conditions there was no propagation, the reaction

ceasing as soon as the sample melted and broke the circuit. The minimum oxygen concentration necessary at other pressures was determined similarly. The results are shown in Table VI and Fig. 10. The curve in the figure is markedly to the left of the

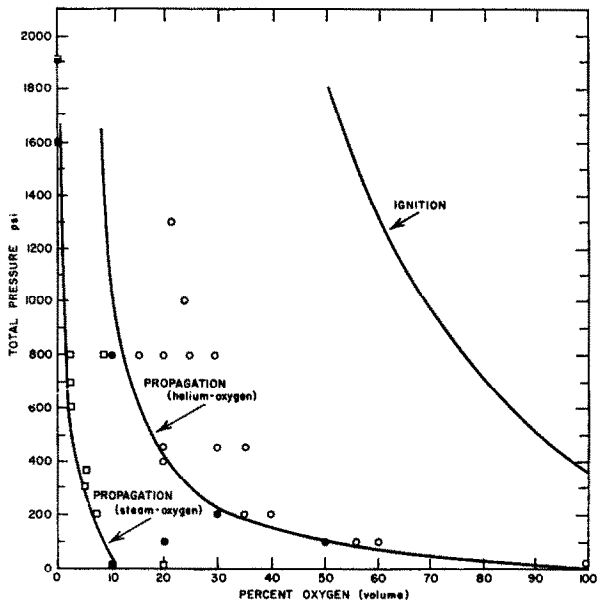

Fig. 10. Ignition propagation in helium–oxygen and steam–oxygen mixtures.

TABLE VI

PROPAGATION OF REACTION OF TITANIUM WITH HELIUM–OXYGEN MIXTURES

O_2 (%)	*He* (%)	P_{total} (*p.s.i.g.*)	*Ignition*
100	—	0	yes
20	(air)	0	no
20	80	100	no
50	50	100	no
60	40	100	yes
55	45	100	yes
30	70	200	no
40	60	200	yes
35	65	200	yes
20	80	400	initial
20	80	450	yes
35	65	450	yes
30	70	450	yes
10	90	800	no
15	85	800	no
20	80	800	initial
25	75	800	initial
30	70	800	yes
25	75	1000	yes
22	78	1300	yes

TABLE VII

PROPAGATION OF REACTION OF TITANIUM WITH STEAM–OXYGEN MIXTURES

O_2 (%)	H_2O (%)	P_{total} (p.s.i.g.)	Ignition
5	95	0	no
10	90	0	yes
20	80	0	yes
7.5	92.5	200	yes
5.0	95	300	yes
5.5	94.5	370	yes
2.5	97.5	600	yes
2.1	97.9	700	yes
20	80	800	yes
10	90	800	yes
2.5	97.5	830	yes
0	100	1600	no
0	100	1900	no

curve delineating the spontaneous ignition limits of titanium in similar mixtures. This indicates that the reaction will continue under much less drastic conditions than were necessary for spontaneous initiation by exposure of a fresh surface.

A similar set of experiments was performed with steam–oxygen mixtures. The pressure vessel was charged with about 100 ml of water, a calculated amount of oxygen was added, and heat was applied until the desired pressure was reached. The reaction was then initiated by passing current through the sample until it melted in the notched area.

The results obtained with steam–oxygen mixtures are quite different from those obtained with helium–oxygen mixtures. As little as 10% oxygen in steam at one atmosphere was enough to sustain the reaction, and at higher pressures less than 5% was needed. Pure steam, however, did not sustain the reaction even at 1900 p.s.i.g. The results are tabulated in Table VII and shown graphically in Fig. 10.

CONCLUSIONS

Some of the limiting conditions for spontaneous ignition of massive shapes of titanium have been defined. From the results presented it appears that relatively massive shapes of titanium will spontaneously ignite if a fresh surface is produced, *e.g.*, by rupturing a sample, in the presence of oxygen under pressure. The mechanism of this reaction is uncertain, but may involve the melting that results from initial reaction. Since the oxide is soluble in the molten metal, no protective surface coating is formed and the reaction becomes self-sustaining. The limiting conditions may be those that generate enough heat during the initial stages of this reaction to melt the surface of the metal.

REFERENCES

[1] J. C. GRIESE, T. M. KEGLEY AND J. L. GREGG, Corrosion of titanium impeller No. 1, *ORNL-CF-55-9-65*, Sept. 1955.

[2] J. P. HAMMOND, T. M. KEGLEY, JR. AND G. M. ADAMSON, Failures of titanium alloy trim in HRP dump valve loop, *ORNL-56-8-214*, Aug. 1956.