Catalysts for Sealed Gas Lasers

PLATINUM METALS ON TIN OXIDE ENSURE LONG LIFE

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Platinum group metals, finely dispersed and supported in porous tin (IV) oxide, have been shown to catalyse the oxidation of carbon monoxide gas even at low ambient temperatures. Such catalysts, recently introduced into sealed carbon dioxide TEA (transversely excited atmospheric pressure) lasers developed at the Ministry of Defence Royal Signals and Radar Establishment, have been a crucial factor in the achievement of prolonged operation of such devices.

Carbon dioxide TEA lasers emit ultra-short pulses of infrared radiation, with a wavelength of approximately 10.6 microns, at extremely high peak powers (~1 MW) in narrow, nearly parallel beams. Examples of their applications include high resolution range-finding and target tracking. Advantages over conventional laser range-finders using wavelengths close to the visible include much better penetration of smoke and fog and far greater eye safety.

Optical gain in carbon dioxide TEA lasers occurs in a pulsed, uniform electric discharge in a carbon dioxide-nitrogen-helium gas mixture at atmospheric pressure. The difficult problem of generating a uniform discharge at this high pressure, is solved by pre-illuminating the entire active volume with ultra-violet (u.v.) radiation from nearby subsidiary discharges fired immediately before the main volume is energised. Each u.v. pulse uniformly pre-ionises the gas throughout the optical gain region and prevents the development of localised arcs.

For minimum system size, the laser must give maximum peak power output per unit discharge volume. This necessitates operation at the highest possible carbon dioxide concentration, up to 60 per cent of the total gas, which in turn makes it harder to maintain a uniform discharge. Operation in these difficult conditions was only achieved if the laser was continually flushed through with fresh gas. However, a device for field use must be capable of prolonged sealed operation without gas replenishment. The principal factor preventing this was the dissociation of carbon dioxide into carbon monoxide and oxygen, low concentrations of the latter rapidly degrading the discharge into localised arcs.

Prolonged operation of a sealed, high-carbon dioxide laser was first reported in 1978 (1). In this device a short length of platinum wire at a temperature of approximately 1100°C continuously catalysed the recombination of carbon monoxide and oxygen. Over 2.5×10^6 pulses were achieved at the modest pulse repetition frequency (PRF) of 2 Hz.

However, for some applications, such as rapid range-finding, PRFs of about 100 Hz are needed. In such cases, the greater generation of carbon monoxide and oxygen requires correspondingly increased catalyst speeds. In these conditions a hot platinum wire would not only consume excessive power but would also create a cooling problem.

Porous Tin Oxide Supports

Clearly, there was a requirement for a catalyst with greatly increased activity, preferably at ambient temperature, which would eliminate the need for both additional heating power and a cooling system. Other workers have shown that platinum or palladium, very finely dispersed and supported in porous tin (IV) oxide would, at temperatures between 82 and 200°C, catalyse the oxidation of carbon monoxide in the presence of a considerable excess of oxygen (2). Their measurements, in entirely different conditions and not directed towards lasers, were made in the absence of carbon dioxide and used 20 per cent oxygen in the presence of 6 per cent carbon monoxide and

74 per cent nitrogen. They showed that the constituents of this combination of stannic oxide and platinum metals acted synergistically, thus activating oxidation rates for carbon monoxide much greater than those due to each component in isolation.

In experiments at the Royal Signals and Radar Establishment several materials including palladium/stannic oxide, platinum/stannic oxide and the best commercial catalyst (Hopcalite), were exposed to typical TEA laser gas mixtures at one atmosphere pressure in a sealed vessel (3). Carbon dioxide concentrations up to 60 per cent were used, the balance being nitrogen and helium. The carbon dioxide was then partially dissociated by firing tungsten arcs just long enough to create carbon monoxide and oxygen concentrations of 6 to 8 per cent and 3 to 4 per cent, respectively. The subsequent carbon monoxide and oxygen removal rates and the corresponding carbon dioxide generation rates were determined by mass spectrometry as functions of catalyst temperature, exposure time and partial pressures of the interacting gases. The experiments were performed with each catalyst at a number of different temperatures between 44°C and −27°C; all demonstrated measurable activities.

The best results were obtained with 1.8 weight per cent palladium and 1.3 weight per cent platinum, each supported on stannic oxide, which showed apparent activation energies of 39.7 kJ/mol (standard deviation 6 per cent) and 41.4 kJ/mol (standard deviation 5 per cent), respectively. For equal masses, the room-temperature activities were nearly a factor of 70 greater than for the best commercial catalyst. Moreover, unlike the commercial catalyst, which rapidly deteriorated, they retained their activity despite repeated exposure to moist air.

Platinum group metal/stannic oxide catalysts have now been successfully used in high-PRF, high-carbon dioxide TEA lasers and prolonged sealed operation of these devices has recently been reported (4). In order to achieve high-PRF operation, a fan drives the hot gases from the electric discharge continuously round a closed loop in which they are cooled before being returned to the discharge region. During circulation, the gases pass between metal plates coated with platinum group metal/stannic oxide catalyst which continuously recombines the carbon monoxide and oxygen generated in the discharge. The catalyst, at an equilibrium temperature up to 50°C, is unheated except by the hot discharge gases and therefore requires neither additional power source nor cooler.

The laser is sealed with a carbon dioxide-rich gas mixture which is typically 50 per cent carbon dioxide–33 per cent nitrogen–17 per cent helium and provides output peak powers of about 1 MW. Over 2×10^7 pulses have been obtained from a single gas fill. Operation is mostly at a continuously applied PRF of 30 Hz, or in regularly repeated bursts of 100 Hz. By contrast, without the catalyst, the laser discharge consistently failed after only 3×10^3 pulses, through the rapid accumulation of excessive oxygen. With the catalyst, on the other hand, the oxygen concentration is maintained continuously below 0.3 per cent throughout the test. There has been no evidence of any deterioration of either the catalyst or the gas discharge which would prevent the achievement of much longer lives.

The use of platinum group metal/stannic oxide catalysts in carbon dioxide lasers is covered by Ministry of Defence patent rights (5).

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