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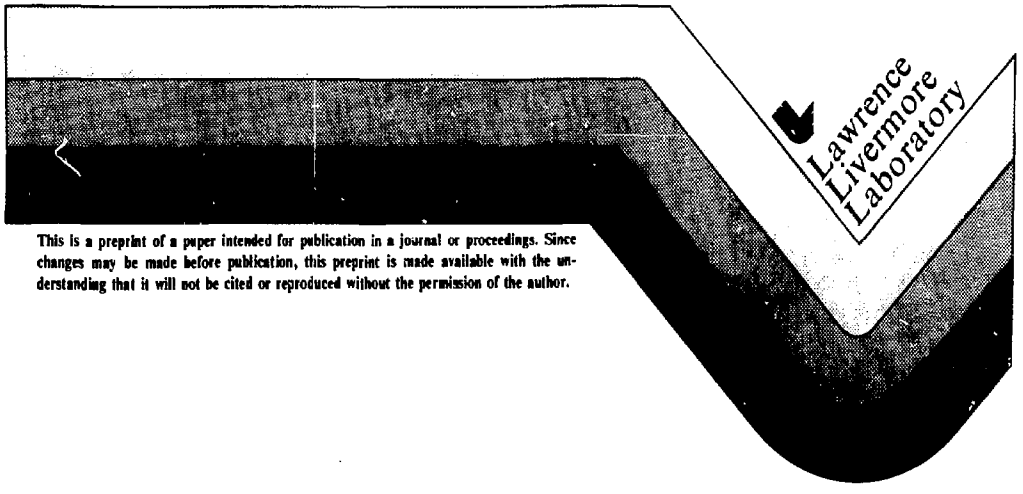

RECENT ADVANCES IN PT COATING OF MICROSPHERES BY A BATCH MAGNETRON SPUTTERING PROCESS*

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ABSTRACT

Some proposed inertial confinement fusion targets require high-Z, high density metal coatings on glass microspheres. Platinum, which satisfies the high-Z and density requirements, can be coated onto microspheres with a batch magnetron sputtering process incorporating oxygen as a dopant gas to prevent the microspheres from sticking. This paper outlines recent progress in three areas: First, the coating process has been improved; second, the oxygen content and resistivity of the oxygen doped platinum films are analyzed; and third, the roles oxygen may play in reducing microsphere sticking during sputtering are discussed in regard to cold welding, Van der Waals bonding, electrostatic sticking, and sintering.

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INTRODUCTION

In proposed laser fusion targets, high Z, high density coatings on glass microspheres are needed as the tamper layer. The development of a batch coating process for coating microspheres with platinum by magnetron sputtering was reported earlier.[1] Platinum, which satisfies the high Z and high density requirements, was chosen for its adhesion to fixturing and its resistance to cold welding upon impact. However, successful Pt coating of microspheres required oxygen doping of the sputtering gas to reduce microsphere sticking during coating.

The oxygen doping during sputtering affected both the material properties of the Pt coating and the mechanisms responsible for the microsphere sticking. Unfortunately, adjusting the oxygen flow to achieve the optimum material properties was often in conflict with alleviating the sticking effects. Hence, better control of the coating process required understanding the roles of oxygen in preventing sticking, and the effect of oxygen on the Pt coatings.

This paper reports on recent progress in three general areas. First, the bouncer process has been improved for operation without the screen formerly required to confine the microspheres in the bouncer. The second section reports on the oxygen analysis of the Pt coating on microspheres by Auger electron spectroscopy, and on the resistivity changes produced by the oxygen doping. The final section discusses several proposed roles for the oxygen dopant in reducing the microsphere sticking problem.

PRESENT MICROSPHERE COATING PROCESS

We have extended our bouncer method to operation without the screen over the bouncer pan previously used to confine the microspheres. The new configuration, shown in Fig. 1, is desirable for increased coating rate, to improve the visibility of the microspheres during coating, and to eliminate occasional flaking from the screen. The resultant Pt coatings, shown in Fig. 2, are as good or better than those obtained earlier. We attribute the better coating to the improved vision, which allows us to make appropriate adjustments on the coating parameters when the microspheres start to clump, and the elimination of possible contamination from the screen. However, in this screenless configuration, the sticking problem can no longer be dealt with by increasing the bouncer drive and applying a large negative bias (-100VDC) to the bouncer. Either positive or negative dc bias on the pan will make the sticking problem more pronounced. At the extreme (> 300 volt), negative bias can induce uncontrollable microsphere motion, and expell the microspheres from the pan. Floating the substrate electrically gives the least sticking.

Bouncing uncoated glass microspheres without a plasma present invariably causes the microspheres to clump, due to triboelectric charging of the non-conducting glass.[2] Such problems are not usually encountered if the microsphere surfaces are conductive, or if the microspheres are exposed to a low power plasma. Without the impediment of the screen, the microsphere motion and any sticking can be clearly observed and immediately corrected. The important factors affecting

their motion are O_2 dopant level, bouncer bias (floating), and conductivity of the microsphere surface. Bouncer drive level, sputtering power and pressure are of secondary importance.

OXYGEN DOPED PLATINUM FILMS

Oxygen Content. We reported earlier on the effect of O_2 on the morphology and grain size of the Pt coatings on microspheres.[1] The microspheres were coated with the screened bouncer pan at a total pressure of approximately 0.9 Pa, 30 SCCM argon flow, and different oxygen flows for each run. Microspheres from these runs were analyzed for oxygen content by Auger electron spectroscopy. To obtain a representative oxygen analysis, the Pt coatings were ion milled until the oxygen peak reached a constant value. The oxygen content varied substantially from one microsphere to the next in the same deposition batch (possibly due to Auger spectroscopy artifact on spherical substrate); however, the batch average oxygen content correlated well with the oxygen doping level during the deposition. The batch average oxygen content is plotted as a function of O_2 doping level in Fig. 3 showing a linear relationship.

The oxygen content data suggest that as the film grows, it traps oxygen adsorbed on the surface at a rate proportional to the partial pressure (which probably determines the surface coverage). X-ray diffraction measurements on both flat slides and microspheres[3] are in agreement with this data. The lattice expansion and line broadening from the X-ray data suggest that the oxygen is incorporated interstitially in

the Pt structure, and not exclusively trapped at grain and column boundaries. This conclusion is supported by the increasing brittleness of the Pt coatings with increasing oxygen partial pressure, as reported earlier.

Resistivity. Early experiments had shown that microspheres coated with oxygen doped Pt would continue bouncing freely in vacuum, in marked contrast to uncoated glass microspheres. However, the introduction of hydrogen gas into the system (without sputtergun power) would cause the microspheres to stick. Evacuating the hydrogen and introducing oxygen would release the clumped microspheres.

To investigate the extent of gas adsorption, we measured the sheet resistance of thin Pt films deposited on glass slides with normal microsphere O_2 doping. The film was kept in vacuum after deposition and its resistance remained constant when low pressure oxygen was introduced. When the film was exposed to hydrogen gas, the resistance dropped markedly, as shown in Fig. 4. After the initial drop in resistance following the hydrogen exposure, subsequent O_2 exposure increased the film resistance, but did not restore the film to the original value. The resistance could be cycled back and forth between the levels corresponding to hydrogen or oxygen adsorption. Films deposited without oxygen doping show little resistance change upon initial exposure to hydrogen gas, but show the same resistance increase with oxygen adsorption. The fact that the resistance does not return to the original value suggests that the hydrogen gas has penetrated and removed oxygen from the bulk of the Pt film, whereas the oxygen is adsorbed only on the surface.

STICKING MECHANISMS AND THE ROLE OF OXYGEN

The microsphere sticking problem seems to include at least four mechanisms: First, cold welding of soft metals; second, Van der Waals bonding of clean metals; third, net charge attraction of non-conducting microspheres; and fourth, polarization attraction of metal coated microspheres in a non-uniform electric field. Finally, microspheres temporarily stuck together during coating may be permanently joined by sintering.

Solid State Bonding. Cold welding of microspheres coated with soft metals such as Al, Cu and Au, has been described elsewhere.[4] A characteristic of cold welding is the formation of a rigid, permanent bond between two surfaces. On microspheres, breaking the cold weld bond should leave a definite scar, often a patch torn out of the coating. We have seen no conclusive evidence of cold welding with Pt coatings on microspheres. If cold welding is a problem with pure Pt, then hardening the coating by oxygen doping should prevent it.

The clumping of Pt coated microspheres with exposure to hydrogen gas, and the quick release of the microspheres by oxygen gas (without plasma) suggests that a second bonding mechanism besides cold welding is involved. The reversibility indicates that this sticking does not involve chemical bonds, but rather is a form of Van der Waals, or induction bond, dependent on close range metal-to-metal contact. The oxygen adsorbed on the Pt surface ties up the conduction electrons reducing the local electronic polarizability, thus freeing the

microspheres. We expect that this Van der Waals bonding would only be a problem for noble metals like Pt, Pd, and Au, and not for more reactive metals like Cr, Ni, and Ti where the deposition system background gases should be sufficient to prevent sticking.

Electrostatic sticking. A more detailed description of electrostatic sticking of microspheres during sputter coating is given elsewhere.[4] However, for completeness, we briefly describe the polarization sticking force, and suggest two possible ways that the oxygen dopant gas might neutralize the sticking mechanism. The sticking is probably due to the electric field in the plasma sheath which exists over the fixturing. The electric field exerts a force on the net charge on a microsphere, and induces a dipole moment in a metal coated microsphere. However, the electric field strength in the sheath is very non-uniform, decreasing rapidly with distance away from the bouncer surface (because of the positive ion space charge), and vanishing at the edge of the plasma sheath. The field gradient will exert an attractive force on the induced dipole in the direction of the stronger field.[5] Moreover, in contrast to net charge attraction, polarization attraction is not neutralized by contact between the microsphere and the fixturing.

On a moving microsphere, the effective dipole moment will be reduced when the dipole relaxation time is comparable to the microsphere reorientation time. The longer dipole relaxation time caused by the increased resistivity of oxygen doped platinum would reduce the effective dipole moment on a rapidly moving and spinning microsphere. Also, the oxygen atoms in the plasma can attach electrons and decrease the mobility

of the negative charge species. The plasma would establish a different electron energy distribution, and could have a significantly different electric field in the sheath region. Since the polarization force is proportional to the product of the electric field gradient and dipole moment, a reduced attractive force would result from a decrease in either the field gradient or in the effective dipole moment on the microsphere.

Solid State Sintering. We also suspect that solid state sintering[6] may turn temporary sticking into permenant bridges between microspheres. The crystalline Pt coating contains high surface free-energy and the natural tendency is for such a system to minimize the surface area. Microscopically, the surface free energy driving term is responsible for suppressing void growth under conditions of sufficient adatom mobility to form zone 2 growth.[7] Macroscopically, the shallow angle crevasse between two microspheres in contact should be filled in by the same process. The material transport is illustrated in Fig. 5, along with a possible example of solid state sintering of two gold coated microspheres. We detected no foreign material by X-ray microprobe in the contact areas. The curvature of the filled in material at the contact point suggests that surface free-energy is involved.

The addition of oxygen into the sputtering gas would reduce the tendency for sintering. It is well known[6] that the adsorption of gases with large ionic radii, such as O^-, greatly reduces the surface free energy of metals. The adsorption of oxygen on a growing Pt coating should reduce the driving force and decrease the adatom mobility necessary for sintering.

SUMMARY

We have reported here an improved batch magnetron sputtering process for platinum coating on microspheres without a confining screen over the bouncer pan. Better yields are achieved with this improvement because of the higher sputtering rate and better visibility. Auger analysis demonstrated a linear increase in oxygen content with doping flow rate, in agreement with the observed increasing coating brittleness. Resistivity measurements on very thin flat films indicated that hydrogen gas can remove the oxygen incorporated in the platinum, and that subsequent oxygen gas will only adsorb on the surface. A direct result of O_2 absorption is an increase in the Pt sheet resistance.

The microsphere sticking mechanisms operating during platinum coating appear to include Van der Waals bonding and polarization attraction in the plasma sheath. Adsorbed oxygen on the coating surface would prevent Van der Waals bonding by competing for the available conduction electrons, while oxygen could reduce the polarization sticking by decreasing the effective microsphere polarization, or by reducing the electric field gradient in the plasma sheath.

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FIGURE CAPTIONS

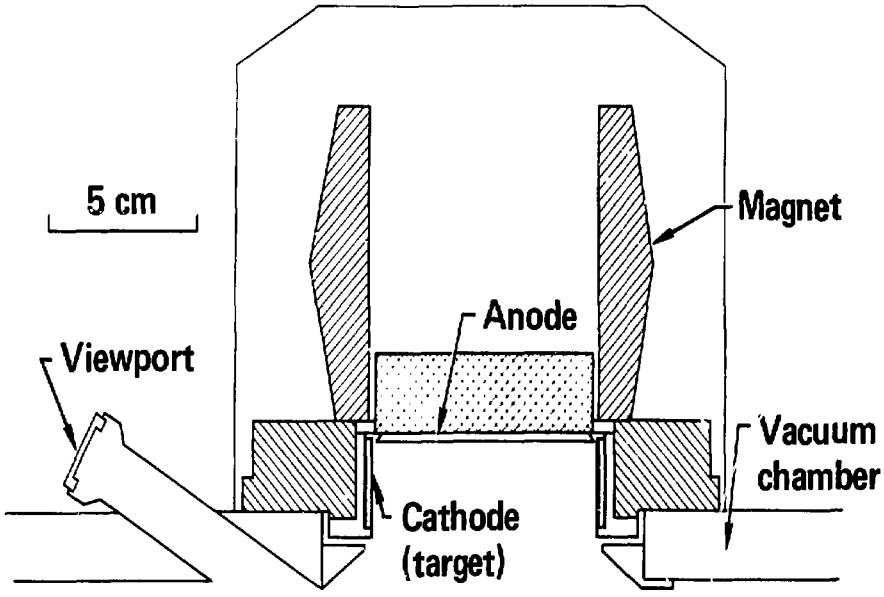
Fig. 1 Schematic diagram of the improved fixturing for batch sputter coating without confinement screen over the bouncer pan.

Fig. 2 Smooth (<100 nm) Pt surface on microsphere coated by the improved batch process.

Fig. 3 Oxygen content of Pt coatings on microspheres as a function of oxygen flow rate during coating. Analysis was performed by Auger electron spectroscopy.

Fig. 4 Schematic representation of Pt film sheet resistance during sequential exposure to oxygen and hydrogen gases.

Fig. 5 Clumped gold coated microspheres suggesting solid state sintering, and schematic diagram of the surface transport involved in sintering.


5 cm
Magnet
Anode
Viewport
Vacuum chamber
Cathode (target)

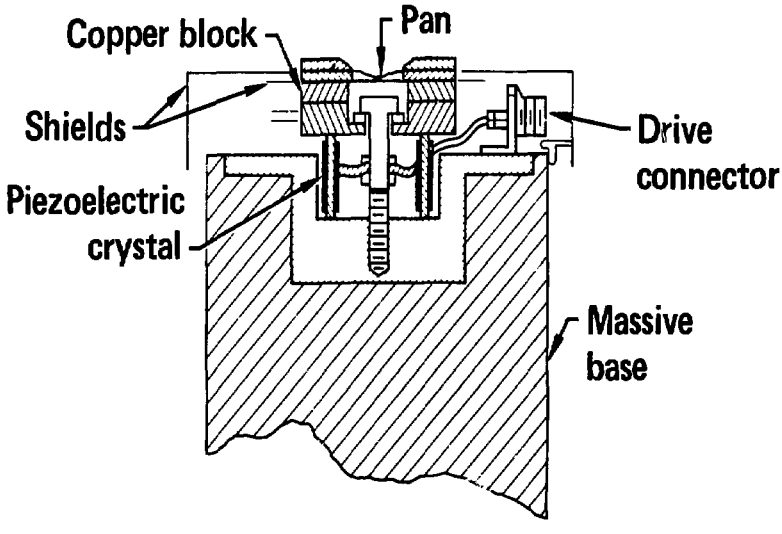

Copper block
Pan
Shields
Drive connector
Piezoelectric crystal
Massive base

FIGURE 1

SMOOTH PLATINUM COATED MICROSPHERE

(a)

30 μm

(b)

1 μm

- 2 μm thick
- 10 mg/cc DT fill
- Surface finish < 100 nm

FIGURE 2

AUGER ANALYSIS OF O_2 IN DOPED Pt COATING ON MICROSPHERES

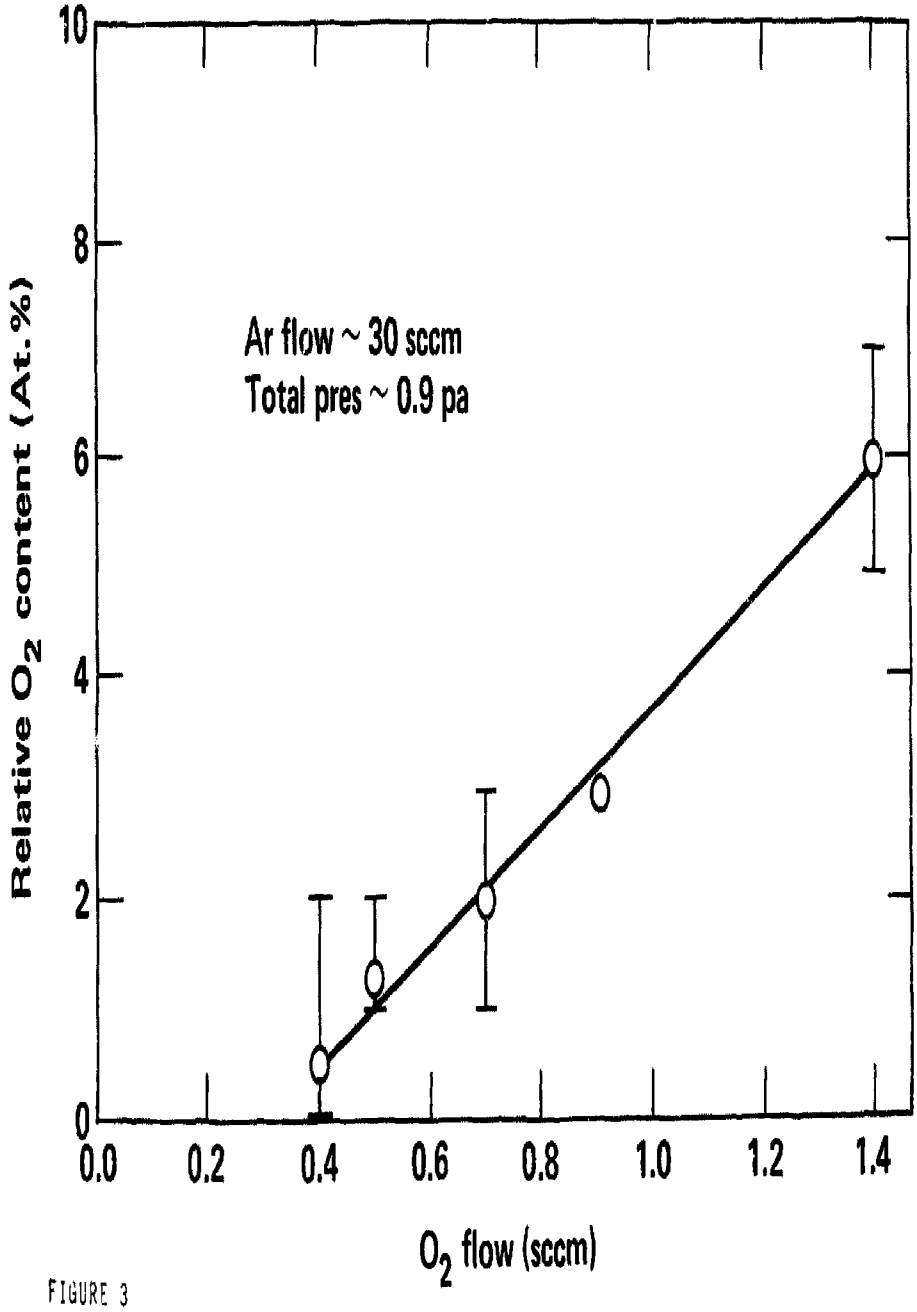


FIGURE 3

SHEET RESISTANCE OF Pt FILM IN RESPONSE TO O_2 AND H_2 CYCLING

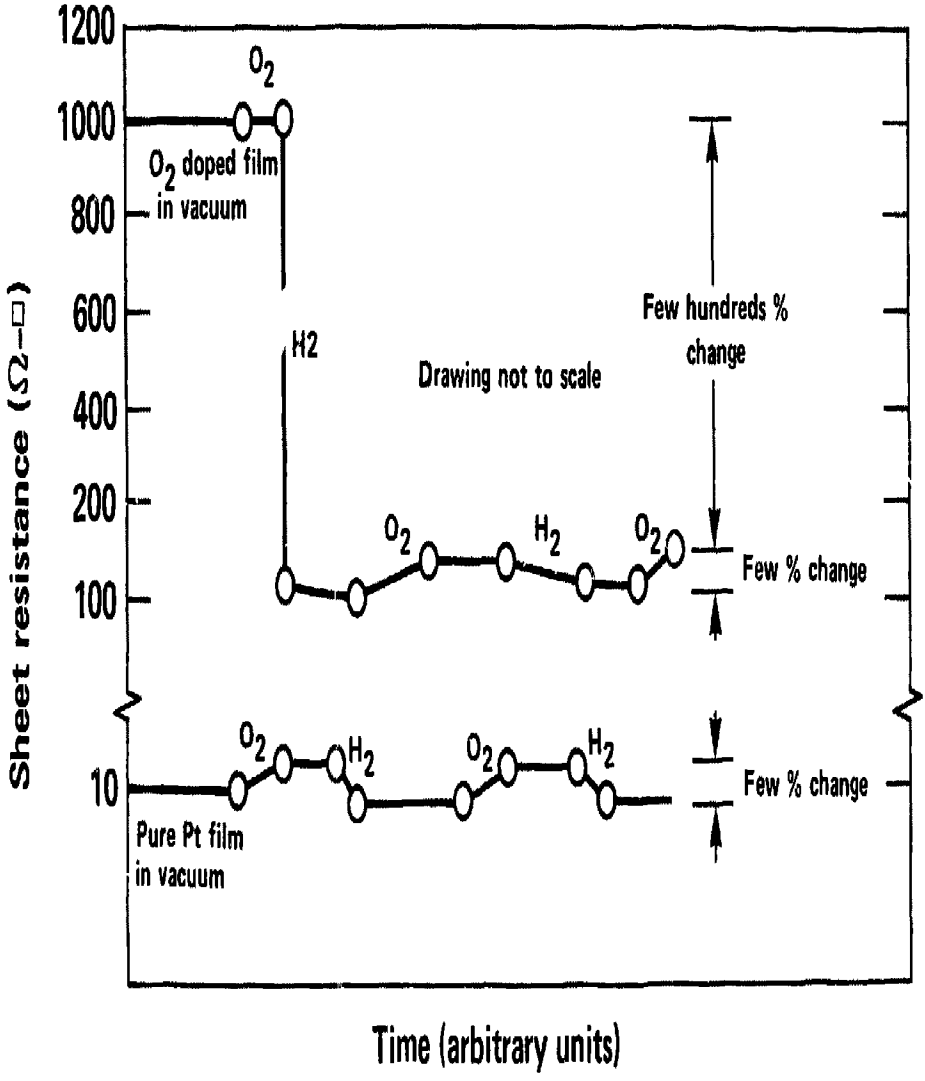
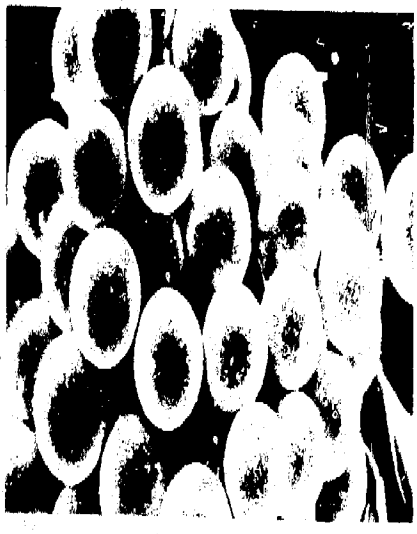
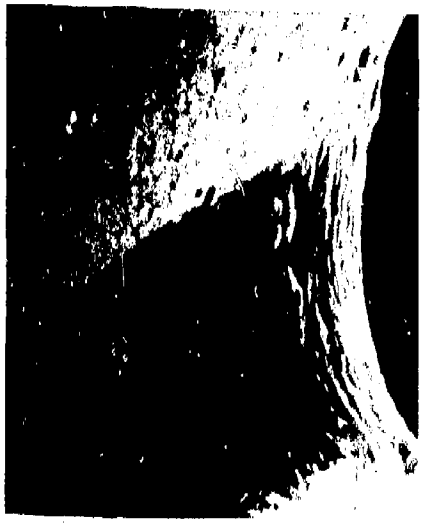


FIGURE 4

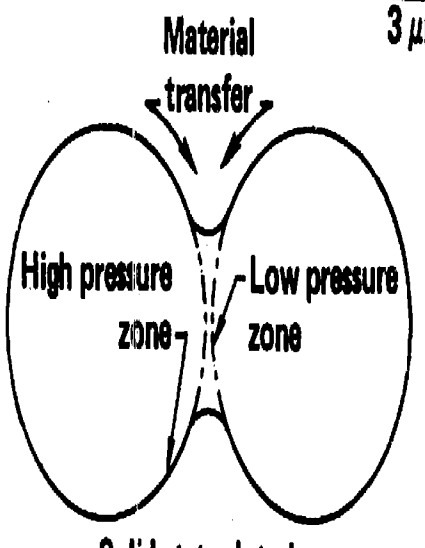
CLUMPED Au COATED MICROSPHERES SUGGESTING SOLID STATE SINTERING



100 μm



3 μm



Solid state sintering

FIGURE 5