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Acid-assisted consolidation of powder compacts: cold-welding or cold sintering

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Silver powder that has been treated in dilute fluoroboric acid solution and compacted at room temperature displays surprisingly elevated flexural and even tensile strength. The density and mechanical strength values increase with increasing compaction pressure. The flexural strength and the elastic moduli of silver powder compacted at 1 GPa, as determined by sound velocity measurements, reach values comparable to those of bulk silver. The results can be tentatively interpreted either in terms of an ambient temperature self-soldering effect of silver in the presence of the fluoroboric acid, acting as a fluxing agent, or as cold liquid-phase sintering in an aqueous liquid medium. © *1999 Kluwer Academic Publishers*

1. Introduction

Conventional powder metallurgy relies on the combined effect of pressure and temperature, applied sequentially or simultaneously, to impart a desired level of mechanical strength to powder compacts. Sintering of the powder particles takes place during the high temperature treatment. The properties of the final product, i.e., strength, conductivity and resistance to wear, depend on the density attained during sintering. The conditions prevailing during processing prior to sintering, such as powder preparation, lubrication and the method of compaction, determine the “green strength” of the compacted material. The green strength correlates with the apparent density of the pre-sintered compact, and in most cases is significantly lower than that of the body after sintering. A detailed parametric study of the mechanical properties associated with the green stage is, in general, of limited interest since the green stage is usually a temporary one.

In the course of a study undertaken several years ago at the National Institute for Standards and Technology (NIST) a situation was encountered in the framework of which exposure of powder compacts to elevated temperature was unacceptable, yet relatively high levels of mechanical strength were required. The powder compacts consisted of silver or silver-rich alloys and were to be used as mercury-free substitutes to directly placed metallic dental restorative materials.

A early approach, inferred from the removal of tin oxide from tin metal, revealed that a chemical surface treatment in an aqueous fluoroboric acid (HBF_4) solution activates the silver powder, and promotes its condensation into a cohesive solid at ambient temperature. Compaction of silver powder samples after the surface treatment, even under low pressure, results in samples that display surprisingly elevated levels of flexural strength that are comparable to that found in existing dental filling materials [1, 2]. The approach was subsequently extended to other applications and to the production of materials compacted at higher pressure, and is now known under a series of designations such as acid-assisted consolidation, acid-induced cold welding, cold forming or cold sintering. These designations refer to the process whereby relatively high-strength products are manufactured at ambient temperature by compaction of the surface-treated powders. High strength is achieved without recourse to subsequent sintering. In this communication henceforth, the process will be designated as the AAC (acid-assisted consolidation) process.

The present paper is aimed at describing the AAC process and to present data regarding the mechanical properties of silver compacts that are produced via this method. The new technique is obviously dependent on a great number of processing and material parameters that may affect the properties of the products. A complete review of these effects is, however, beyond the scope of this paper. The results that are presented in the following section are meant to illustrate the potential of this novel technique. Emphasis is placed on the attainable mechanical properties of the silver compacts obtained by this approach; properties that are truly striking when compared to those found in materials produced by conventional ambient temperature compaction.

2. Experimental

The silver powders that were examined and treated by AAC covered a range of particle or agglomerate sizes from 0.1 to 80 μm, were of different origin, produced

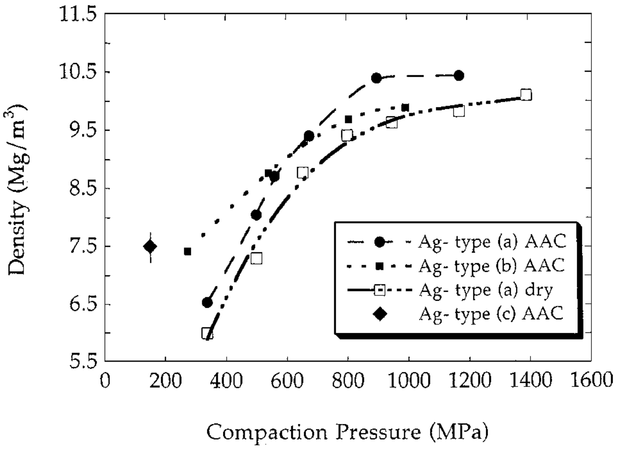

Figure 1 The density vs. applied compaction pressure of silver samples. Type (a) refers to atomized silver particles after AAC or to the same particles compacted as dry powder; type (b) is ultra-fine, sub-micron size silver particles after AAC. Type (c) powder refers to hand-consolidated precipitated silver after AAC. The density values shown have a standard uncertainty of 0.02 Mg/m^3.

by atomization, chemical precipitation solution or by electrodeposition, and had spherical, dendritic or other irregular shapes. In some instances the silver powder was annealed prior to its compaction in the 300 to 450 °C temperature range under argon or in air.

The results that are presented were obtained mainly using atomized silver powder with 5 to 10 μm average particle size. Some results (Fig. 1) were obtained using sub-micron size fine powders that were manufactured by the polyol process [3], and had an average grain size of 1 μm. Powder ‘150’, used mainly for hand consolidation, was prepared by precipitation and consisted of irregularly shaped agglomerates with 1 μm particle size [4].

The AAC process consisted of activating the silver powder by submerging it in a 10% volume fraction HBF_4 (dilution from a 48% mass fraction of HBF_4) solution in a glass beaker, and stirring with a slowly rotating overhead stirring paddle for 1 min. The powder particles were allowed to settle for several minutes, and the acid was decanted leaving behind the settled powder as a wet slurry. In most instances, the slurry was rinsed in a second more dilute solution, 2% volume fraction HBF_4.

Compaction of the silver slurry was performed manually with hand dental instruments in order to simulate actual dental procedures in the low pressure (<100 MPa) range, or in a hydraulic press for higher (100 MPa to 1 GPa) pressures. The compression was done in appropriately shaped plastic or steel molds. The shape of the silver compacts was determined by the properties to be tested. Disc shaped samples between 8 to 20 mm diameter and 1.5 to 3 mm high were prepared for hardness, compressive strength and elastic moduli determinations. Bar shaped specimens were manufactured for transverse rupture strength measurements. The specimens consolidated in the low pressure range were fabricated by incrementally compacting slurry portions in the mold using a 1.5 mm diameter serrated dental amalgam condenser either manually or with pneumatically assisted instruments. The estimated compaction pressure at the instrument tip was of the order of 10 to 50 MPa. In the high pressure range, the slurry was compressed by appropriately shaped steel plungers. During compaction, the excess acid solution was squeezed out and blotted from the mold with paper tissue.

The silver compacts consolidated in steel molds and compressed by steel plungers had smooth surfaces, and did not need further surface preparation. The hand consolidated samples were polished on silicon carbide paper to a finish of 600 grit.

In most instances the density was determined from the weight and the geometrical dimensions of the samples. The density of samples used for the elastic constant measurements was determined by the fluid displacement method. This method also allowed determination of the open and closed porosity of the samples. Compressive strength was determined using 4 mm diameter cylindrical specimens. Transverse rupture strength was measured on a three point bending fixture with a fulcrum spacing of 10 mm using an Instron universal testing machine. The load was applied to the center of the sample at a constant cross-head speed of 1 mm/min until failure. A few tensile specimens were also compacted, and the tensile strengths were determined at 0.5 mm/min cross-head speed. The results that are reported represent averages obtained on lots of four to six samples prepared under identical conditions.

The elastic constants of the compacted silver were determined from ultrasonic sound velocity measurements carried out on the compacted cylinders. The samples were 8 mm diameter, 1.5 to 2.5 mm thick cylindrical discs that had been compacted to net shape and had plane parallel faces. The ultrasonic measurements were performed using 5 MHz longitudinal and shear wave quartz transducers. The transducers were excited by timed pulses from an ultrasonic pulse receiver. The time-of-flight measurements for the ultrasonic signals were performed using the pulse-echo overlap method on a digital oscilloscope. The sound wave velocity was determined by measuring the sample thickness with a micrometer, and dividing the pathlength (twice the thickness) by the time of flight. Care was taken to avoid contamination of the porous samples by the couplant. Each datum point represents the average of several independent measurements.

3. Results

3.1. Density

The results of numerous trials carried out on several different silver powder compacts are shown in Fig. 1. As expected, density appears to be directly related to the compaction pressure with a near-linear relationship. Very little difference can be observed between dry compacts and compacts made in the presence of the activating acid. One exception to this relationship is the ‘Type c’ powder, which displays a relatively elevated density value at 150 MPa of compaction pressure. That particular powder is made of near-micron size precipitated silver particles, and is currently the leading contender for dental applications.

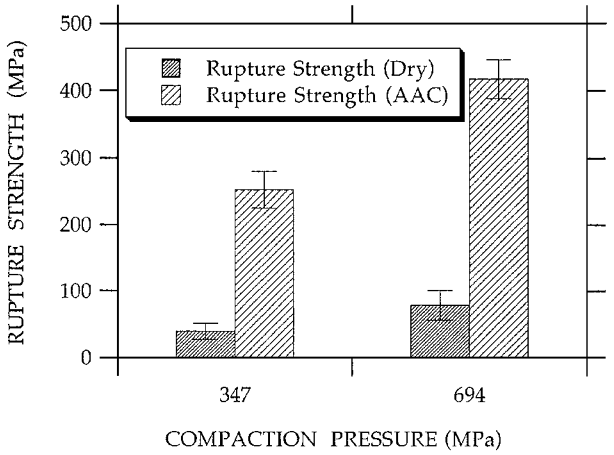

Figure 2 Mean and standard deviation of transverse rupture strength values of compacted silver powder. The figure illustrates the effectiveness of the AAC process in providing significantly enhanced green strength to compacted silver powder after AAC. One standard deviation is given as an estimate of the total combined standard uncertainty of the measurements.

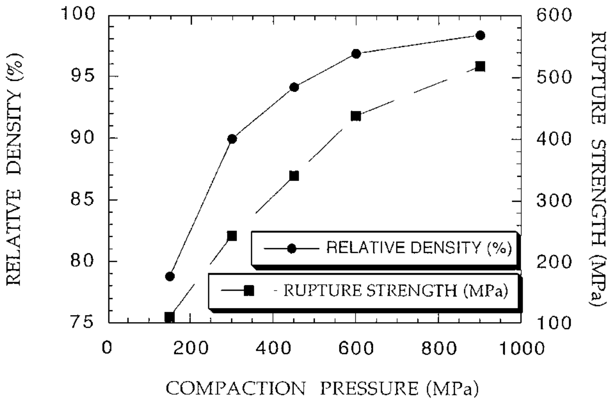

Figure 3 The relative density and transverse rupture strength of atomized silver powder compacts as a function of the compacting pressure. Each point represents the mean of four to six samples.

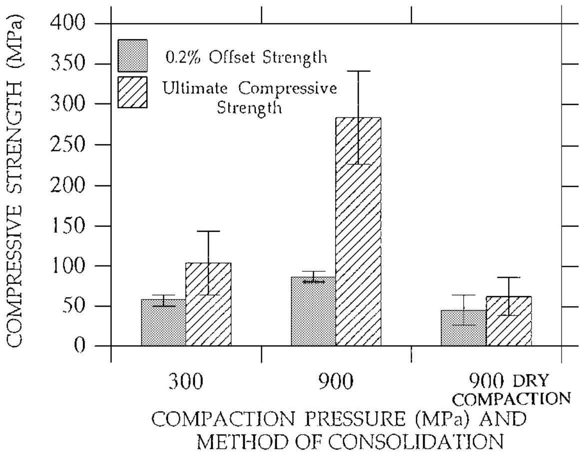

Figure 4 The means and standard deviations of the compressive strength of compacted silver powder after AAC. Noteworthy is the extended plastic range of silver powder compacted at high pressure after AAC.

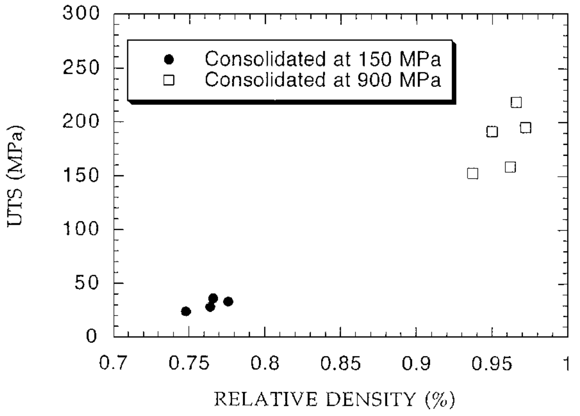

Figure 5 The tensile strength and density of silver powder compacts after AAC at 150 and 900 MPa, respectively. Each data point is the result of one measurement.

3.2. Transverse rupture, compressive and tensile strength

Transverse rupture strength is the property most commonly used to evaluate the mechanical strength of compacted powder specimens in their unsintered green state. The striking effect of the AAC process is illustrated in Fig. 2, which shows a 5-fold increase in rupture strength of a silver compact after AAC as compared to a compact of the same powder under dry conditions. The rupture strength is, as expected, a sensitive function of the compacting pressure and levels out after approximately 900 MPa, as shown in Fig. 3.

AAC also affects the compressive strength of silver, though not as dramatically as the rupture strength. Fig. 4 compares the change in compressive yield and ultimate strength at two different compaction pressures. It is evident from this figure that AAC increases both the compressive yield and ultimate strengths. High pressure compacts resulted in a much larger degree of plastic yield, as demonstrated by the large difference between the yield and ultimate strengths.

Surprisingly, the tensile strength of AAC consolidated silver reaches high values (Fig. 5). This is in particularly significant if one remembers that dry silver powder, even compressed at very high compression pressure, has virtually no transverse rupture strength at all. It is noteworthy that the tensile strength, of the order of 200 MPa, observed for samples compacted at 900 MPa, falls between the values reported for bulk annealed silver (125 MPa) and for 80% cold worked silver, 350 MPa [5]. The fracture surface of a tensile specimen that had been AAC compacted at 150 MPa, is shown in Fig. 6. At that relatively low compacting pressure the contact area between adjacent particles is limited, yet these contact areas clearly present the characteristic features of ductile fracture.

3.3. Elastic properties

The elastic properties of partly sintered powder specimens have been the subject of numerous investigations [6, 7]. In most instances the elastic constants were determined on the basis of sound velocity measurements. Actually, sound velocity measurements can be performed with relative ease, and have been suggested as a means of on-line control of the sintering process. In most reported cases, sound velocity was determined only after the samples had undergone some partial sintering. The scattering of sound waves makes it difficult to carry out measurements on unsintered samples, in

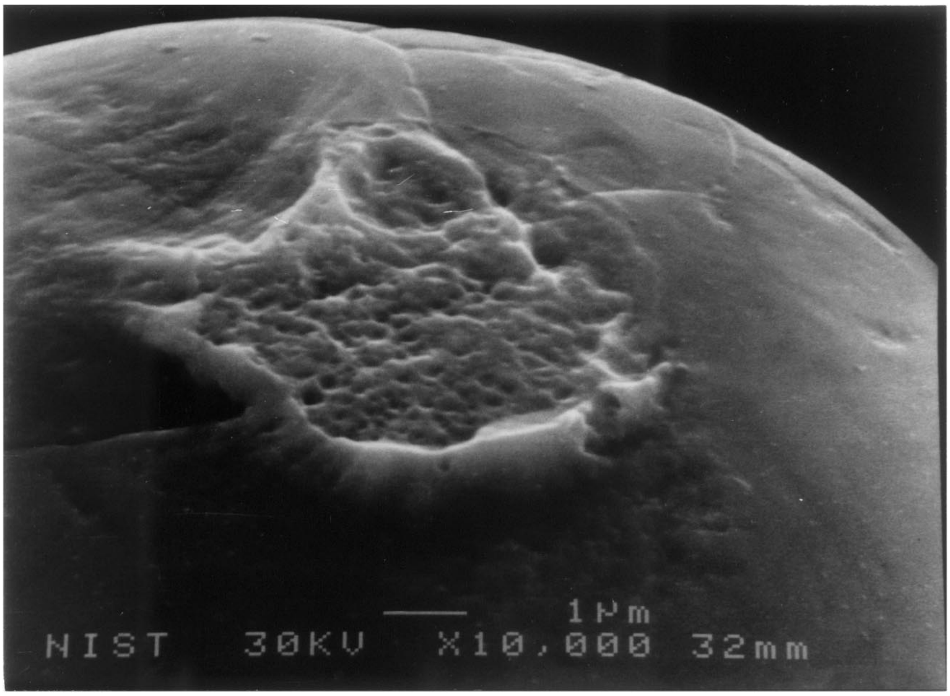

Figure 6 Scanning electron micrograph of the fracture surface of a silver powder sample that had undergone AAC at 150 MPa showing a ductile fracture, indicative of interparticle atomic bonding due to cold-welding.

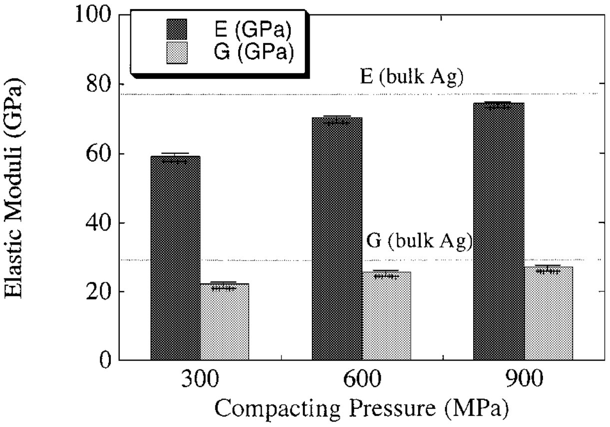

Figure 7 The elastic moduli (mean and standard deviation) of silver compacts as determined from ultrasonic sound velocity measurements as a function of the consolidation pressure.

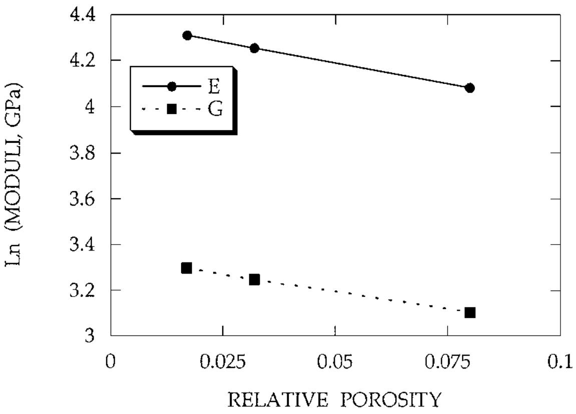

Figure 8 The functional dependence of the elastic moduli of silver compacts after acid-assisted consolidation on their residual porosity. The values shown are the means of three samples with an estimated standard uncertainty of 5%.

particular if they were compacted at low pressure. After AAC, however, it became possible to determine longitudinal and transverse sound-wave velocities even in silver powder compacts compressed at low (<150 MPa) pressures.

Results are shown in Fig. 7 for silver powder compacts consolidated at 300, 600 and 900 MPa pressures. All samples that had AAC, even those at the lowest pressure, yielded sharp sound echoes that allowed easy and accurate determination of the sound velocities. This was in marked contrast to silver samples that underwent dry consolidation. The latter samples, even when consolidated at the highest 900 MPa pressure did not yield any sound echoes whatsoever. The average Young and shear moduli, as determined from the sound velocities in the samples after AAC are shown in Fig. 7. The value of the Young modulus of bulk silver reported in the literature is 78 GPa and the shear modulus is 28 GPa. Thus, the values of the elastic moduli of these unsintered silver samples AAC compacted at 900 MPa closely approach the bulk values.

Phenomenological models link elastic moduli to the density or the porosity of sintered or partly sintered samples [8, 9]. One commonly reported functional form is $M = A \exp(-\alpha P)$, where M stands for the modulus, A and α are material-dependent constants and P is the porosity. In the limited range that was examined, the results that were obtained fit this functional dependence very well, as shown in Fig. 8. Most models, however, depend on the details of the sintering mechanism and other factors. In the present case it is possible to measure the elastic moduli of silver compacts over practically the whole porosity range, yet without the need to sinter. It is of interest to extend the range of validity of this expression to higher porosity, i.e., lower consolidation pressure values.

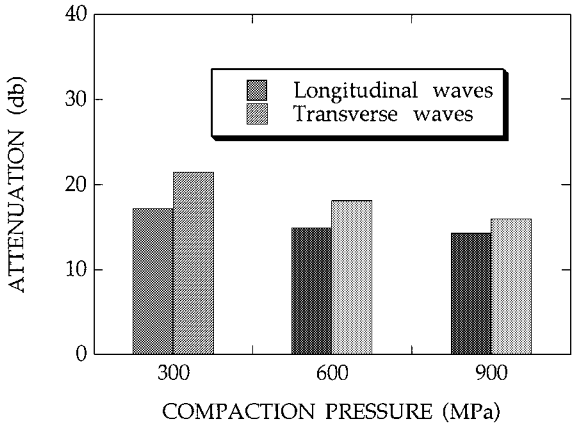

Figure 9 The attenuation of longitudinal and transverse sound waves in silver powder samples after acid assisted consolidation at different consolidation pressures. The attenuation values shown are the median of three measurements on the same specimen.

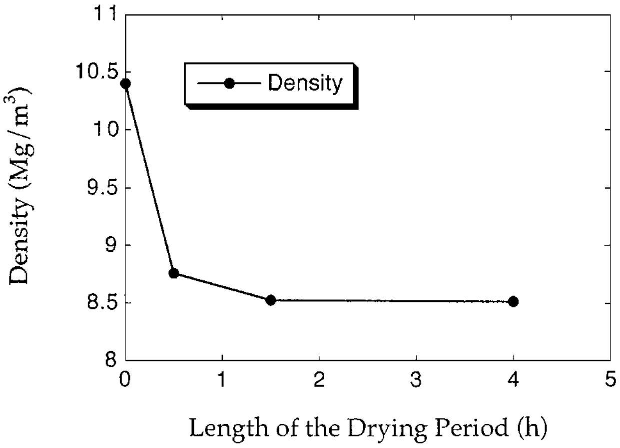

Figure 10 Reduced green density of samples compacted from powder that underwent acid treatment and subsequent drying before being compacted at 900 MPa. The values shown are single measurements with a standard uncertainty of 0.02 Mg/m^3.

Well-defined sound echoes that were observed in the samples that underwent AAC allowed the determination of the attenuation of both the longitudinal and transverse sound waves with relatively good accuracy. The attenuation is given by expression

$$\alpha_{\mathrm{db}} = 20 \log\left(\frac{A_n/A_{n+1}}{l}\right)$$

where α is the attenuation expressed in db, A_n and A_{n+1} are the amplitudes of two consecutive pulse peaks and l is the thickness of the sample.

The results summarized in Fig. 9 clearly reveal consistent behavior patterns. For all compaction pressures, the attenuation of the transverse sound waves was higher than that of the longitudinal waves. This attenuation decreases with increasing compaction pressure. These results were not unexpected, of course; the unexpected element was the high quality of the experimental data obtained on unsintered ‘green samples’.

The possibility of carrying out accurate sound velocity measurements on unsintered silver specimens after AAC significantly strengthens the cold-welding model. It also opens exciting possibilities for studying the relationship between elastic properties and the density of porous samples. From the standpoint of the dental materials, it seems important to extend these studies to the range of low compression pressures (100 to 300 MPa), the range that is more relevant to dental practice.

3.4. Limited duration of the acid-treatment

The acid treatment of silver powder has an effect of limited duration. Powder samples that were dried after the acid treatment for 0.5 to 4 h in open air before compaction rapidly lost the attributes of AAC, as shown in Fig. 10. After 30 minutes of air exposure, the density of compacts returned to approximately that of compacts made from untreated powders.

4. Discussion

The strength of unlubricated green compacts is attributed either to the effects of atomic, electrostatic, Van der Waals forces or to mechanical interlocking of particles. Formation of metallic contacts (cold welding) between neighboring particles is promoted by plastic deformation that occurs during compaction and requires that the surface layers in contact be atomically clean. It is well known that only thoroughly cleaned surfaces provide the necessary conditions for cold welding of two metallic parts that are brought in contact. This indeed occurs during the compaction of pure gold powder into a cohesive solid after the surface-adsorbed gas layers have been desorbed.

The state of the particle surface is an important factor that affects both green strength and subsequent sintering consolidation. Oxide films, present on the surface of particles prevent the formation of metallic bonding at interparticle contact points [10]. For example, it is very difficult to obtain a satisfactory density of compacted aluminum powder, due to the high affinity of aluminum to oxygen. With the exception of gold, all metals exposed to ambient atmosphere are covered by a surface oxide layer that prevents the formation of metallic bonds between adjacent particles. A comparison of oxidized and oxide-free copper particles shows a significant difference in the strength of the compacts. On the other hand, formation of metallic bonds is more likely for powders having less affinity to oxygen or weaker oxide films that can be broken during plastic deformation of the particles, as was observed for iron powder specimens [11]. Thus, sound velocity can be measured with relative ease in iron powder that was compacted at relative low pressure [12, 13], but cannot be done on silver that was compacted as dry powder.

The relatively high rupture-strength values, characteristic of bulk silver, and the unscattered passage of sound waves that were observed in silver compacts after AAC suggest that the surface treatment succeeds in eliminating the surface oxide layers (and other absorbed species) and promotes metallic bond formation throughout the whole powder compact.

The formation of permanent metallic bonds between thoroughly cleaned surfaces is the characteristic feature of metal joining processes, including that of “hard” soldering or brazing. Soldering is defined as a process that generates a permanent bond between metallic parts by means of a metallic filler, the solder, introduced in a liquid state between the surfaces to be joined. Capillary forces cause the liquid to fill the gap between the parts to be joined. Fluxing agents play an important role in the soldering process. They are used to protect the surfaces to be joined from chemical interaction with the environment and to clean these surfaces and the solder from impurities. They also serve to reduce the surface tension of the molten solder on the solid surface. Silver and silver alloys are well-known solders widely used for joining copper alloy or steel metallic parts. It is particularly noteworthy that alkali metal fluroborates such as $NaBF_4$ and KBF_4 are fluxing agents commonly used with silver solders [14]. In conventional silver soldering, the temperature has to be raised above the melting point of the fluxing agents and of the silver solder in order to produce, after subsequent cooling, a permanent joint.

In the context of soldering processes, the AAC process can be viewed as a particular case of silver soldering that can be denoted as ‘cold-soldering’. Silver surfaces are being joined without the need of a molten solder. The metal contact is promoted by the compressive forces and the fluoroboric acid, HBF_4 acts as fluxing agent. This ensemble constitutes a particularly favorable system that allows dispensing with high temperature and the melting of one of the constituents but leads, nonetheless, to the formation of interparticle silver-silver metallic bonds. By definition, however, the soldering process involves the presence of a molten metal. In its absence, ‘cold-welding’ is apparently a more appropriate term to describe the AAC process.

The silver compacts after AAC display most of the characteristic mechanical features of sintered silver specimens. Sintering involves mass transport and formation of interparticle necks at the contact points between particles, and ultimately leads to high density. In the present case, close to theoretical density is achieved by compression in the 1 GPa pressure range at ambient temperature. At ambient temperature, no significant mass transport can take place via solid state, surface or bulk diffusion. If mass transport is a necessary factor to achieve bulk-like mechanical properties in silver compacts, an alternative to solid state diffusion could be a dissolution-precipitation mechanism taking place in the aqueous liquid medium. The fluoroboric acid in contact with silver would presumably be the medium in which some silver mass transport occurs. In this connection it is noteworthy that the exchange currents of silver in a series of acids have extremely elevated values [15]. At the present stage, there is no unambiguous evidence yet supporting this explanation. Were it to be a viable model it would constitute a particular case of liquid-phase sintering taking place in an aqueous liquid medium.

The two models that have been put forward are not necessarily mutually exclusive. Thus, limited dissolution of the base metal in the molten solder and/or fluxing solutions is known to take place in some instances. Preliminary indicate that the AAC process is not confined to the consolidation of silver. Work is in progress to further the understanding of this potentially very useful behavior.

5. Summary

Silver powder irrespective of particle size and morphology can be consolidated in cohesive solids after treatment in a dilute fluoroboric solution compaction even at low pressure. Room-temperature compaction at 1 GPa produces silver compacts that display density, flexural strength and elastic constant values that are characteristic of bulk silver metal.

The results can be accounted for in terms of a self-soldering effect according to which the fluoroboric acid acts as a fluxing agent that cleans and removes the silver oxide surface layers and thereby promotes metallic bond formation between the silver particles. Contrary to conventional soldering no molten metal is involved in this process.

Alternatively and tentatively, some silver mass transport takes place via a dissolution and precipitation mechanism in the aqueous liquid medium. Mass transport, in conjunction with the surface cleaning, promotes cold sintering effects, and leads to the formation of the relatively high strength cohesive solid.

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Certain commercial materials and equipment are identified in this paper to specify the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Institute of Standards and Technology or the ADA Health Foundation, or that the material or equipment identified is necessarily the best available for the purpose.

References

1. M. P. DARIEL, D. S. LASHMORE and M. RATZKER, *Powder Metall.* **37** (1994) 88.
2. M. P. DARIEL, U. ADMON, D. S. LASHMORE, M. RATZKER, A. GIUSEPPETTI and F. C. EICHMILLER, *J. Mater. Res.* **10** (1995) 505.
3. L. K. KURIHARA, G. M. CHOW and P. E. SCHOEN, *NanoStructured Materials* **6** (1995) 607.
4. C. E. JOHNSON, NIST Patent Disclosure, “Precipitation of Silver Powder by the Two Solution Method,” 1998.
5. Metals Handbook, 10th ed., Vol. 2, edited by S. R. Lampman and T. B. Zorc (ASM International, 1990).
6. A. K. MAITRA and K. K. PHANI, *J. Mater. Sci.* **29** (1994) 4415.
7. E. A. DEAN and J. A. LOPEZ, *J. Amer. Ceram. Soc.* **66** (1983) 366.
8. L. P. MARTIN, D. DADON and M. ROSEN, *ibid.* **79** (1996) 1281.

9. R. W. RICE, *ibid.* **76** (1993) 1801.
10. K. E. EASTERLING and A. R. THOLEN, *Powder Metall.* **16** (1973) 31.
11. J. A. LUND, *Int. J. Powder Metall.* **18** (1982) 2.
12. J. P. PANNAKAL, H. WILLEMS and W. ARNOLD, *J. Mater. Sci.* **25** (1990) 1397.
13. A. LER. DAWSON, L. PICHÉ and A. HAMEL, *Powder Metall.* **39** (1996) 275.
14. N. F. LASHKO and S. V. LASHKO-AVAKYAN, “Brazing and Soldering of Metals,” Israel Program for Scientific Translations, Jerusalem, 1961, pp. 142–145.
15. N. A. SHUMILOVA and G. V. ZHUTAEVA, in “Encyclopedia of Electrochemistry of the Elements,” edited by A. J. Bard, Vol. VIII (Marcel Dekker, NY, 1974).

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