THE GRAPE CLUSTER, METAL PARTICLE 63344,1

J.I. GOLDSTEIN

Department of Metallurgy and Materials Science, Lehigh University, Bethlehem, Pa. (USA)

H.J. AXON

Department of Metallurgy, University of Manchester, Manchester (Great Britain)

and

S.O. AGRELL

Department of Mineralogy and Petrology, Cambridge University, Cambridge (Great Britain)

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Metal particle 63344,1 consists of hundreds of metallic globules welded together to form a structure somewhat like a bunch of grapes. It is the largest lunar metal sample found to date, over 5 mm in its longest dimension. Silicate material is attached to the outside of the sample and consists mainly of glass and fragments of An-rich plagioclase derived from a regolith composed of fragments of highland-type rocks.

The globules are all of the same composition (6.25 wt.% Ni, 0.35 wt.% Co, 0.8 wt.% P and Fe) and were produced at the same time and from the same source. No primary solidification structure was observed in the globules. A Widmanstätten pattern of kamacite in taenite and a precipitation pattern of phosphides, which were equilibrated to a temperature of \(<600^\circC\), also developed in the metal. The metallographic evidence indicates that the particle was slow cooled from the solidification temperature \((\sim1300^\circC)\) taking days to possibly months to reach \(600^\circC\).

Two possible mechanisms are proposed for the formation of the globules of 63344,1. One mechanism involves the primary impact of an iron meteorite which produces a metallic liquid and vapor phase. The second mechanism involves the formation of a liquid pool of metal after impact of an iron meteorite projectile followed by a secondary impact in the liquid metal pool. Both mechanisms call for special conditions and sequences of events in order to form a chemically coherent cluster of metal globules uncontaminated by silicates. These globules may adhere after partial solidification and the particle may be slow cooled by burial 0.5–5 m deep in the original ejecta blanket.

1. Introduction

The metal particles that are encountered in lunar rocks and soils often provide quantitative information about the low-temperature thermal history of those rocks and soils. In addition they provide valuable clues to the amount of meteoritic material that has bombarded the lunar surface and the process by which this metal interacts with and eventually becomes incorporated in the lunar rocks and soils. In previous investigations very few metal particles larger than 1 mm have been reported. This paper reports on the largest metal particle found to date (63344,1). It is approximately 1/2 cm in its largest dimension and consists of hundreds of metallic globules that are welded together to form a structure somewhat like a bunch of grapes.

2. Method

Grape cluster metal particle 63344,1 was studied initially, using instrumental neutron activation, by
Haskin [1]. The concentrations of Ni, Co and Fe obtained are 6.9 wt.%, 0.4 wt.% and 91 wt.% respectively. Spectra were also recorded for Au, W and Ir. The low intensities for Na and Mn indicate little contamination by silicate materials.

In this study, the metal particle was examined initially using the scanning electron microscope (SEM), electron microprobe and an optical microscope. The sample was then mounted in epoxy, polished, and examined metallographically with the optical microscope in the reflected mode and the SEM. Electron microprobe analysis for Fe, Ni, Co, P and S in the metal was carried out using wavelength dispersive detectors. Silicate analyses were obtained using an energy dispersive detector and the data reduction technique of Statham and Long [2,3].

3. Results

Metal particle 63344.1 was found in the Apollo 16 coarse fines (4—10 mm) and was described by Marvin [4] as a unique particle consisting of metal globules. There are about 400 metal globules in a restricted size range from 150 to 600 \( \mu \text{m} \) in diameter welded...
together into a cohesive mass (Fig. 1a, b). Fig. 1a shows the composite particle or cluster before sectioning as observed from the side and Fig. 1b and c show it as viewed from the top. The pale material which fills in between the globules (Fig. 1a) is fine dust and consists of 10–100-μm fragments of plagioclase crystals and very fine-grained anorthositic-rich rocks. The sample measures 5.9 mm top to bottom, 5.6 mm across (Fig. 1a) and about 5.6 mm from front to back (Fig 1b). It is by far the largest metal specimen found to date on the lunar surface.

No micropits or vapor-formed crystals were observed by SEM examination. Therefore the specimen has had no exposure to pit-forming high-velocity bombardment after formation. Some of the constituent globules were quite spherical while others were distorted. Fig. 1c shows an enlargement of some of the globules near the top of the particle which are free of plagioclase crystals. Apparently some of the globules have become detached from one another. Some of the surfaces where the globules became detached can be observed in Fig. 1c. The material between the globules is mainly Fe–Ni metal containing phosphide, \((\text{Fe–Ni})_2\text{P}\), schreibersite and small amounts of sulfide, FeS, troilite. Apparently sulfide and phosphide eutectic-type material, having the lowest melting point, solidified last at the outside of the attached globules and helped weld them together. This phosphide eutectic-type material appears to be at most only several microns in thickness.

After surface examination the sample was mounted in lucite. It was oriented in the position shown in Fig. 1a so that its top was close to the surface of the lucite. The mount was ground down to expose the globules at the top of the specimen (note Fig. 1b,c).

Fig. 2a shows the microstructure of the 24 globules exposed in this section, called section A. The central area of section A contains no globules. Fig. 2b shows the microstructure of the specimen after it was ground down ~1 mm from the top surface, called section B. The globules remain loosely packed together although the central area is now filled with metal. No silicate was observed within or between any of the metal globules in sections A or B or in a third section C, about 1/4 mm below section B. Very few of the globules are really spherical and most of them appear to be sintered together and/or plastically deformed (note Fig. 2b). Between the globules

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Fig. 2. (a) Photomicrograph of globules in section A. Field of view is 5.5 mm X 4.2 mm. The black background is lucite mounting material. (b) Photomicrograph of globules in section B. Field of view is 5.5 mm X 4.0 mm.
are Fe–Ni metals with thin platelets of phosphide, the eutectic-type material discussed above which helps weld the globules together. At the junctions between several globules large pieces of troilite, FeS, are also found.

Measurements of the bulk compositions of over 12 globules in section A were made on two separate occasions. The globules were analyzed by sweeping the electron beam over several 50 × 40 μm² areas in each globule. The average composition of all the globules is 6.25 ± 0.2 wt.% Ni, 0.37 ± 0.04 wt.% Co, 0.80 ± 0.1 wt.% P and 92.5 ± 2 wt.% Fe. All globule compositions fall within these limits. Considering all the errors (both statistical and sample dependent) inherent in the determination of bulk composition with the microprobe in globules with varying microstructures, the individual globules are all judged to be of essentially the same composition but with minor variations of P content. It is clear that the globules are chemically similar and were probably produced at the same time and from the same source.

Microstructural examination of individual globules in the three polished sections showed no evidence of dendritic or primary solidification structures. The microstructure of globule No. 20, section A, is shown in Fig. 3a. An outline of the Widmanstätten growth pattern of kamacite, α bcc phase, is apparent. All the fine precipitates are phosphides as shown by microprobe analysis. Fig. 3b is a scanning electron microscope picture of one of the Widmanstätten plates, the boundary of which is decorated with micron-sized phosphides. Measurements of local compositions in phosphide-free areas both within and outside the Widmanstätten pattern give values very close to the bulk composition of globule No. 20, 6.1 wt.% Ni, 0.8 wt.% P. The kamacite-α matrix is, however, depleted in Ni and P close to the phosphides. This depletion arises from diffusional growth of the phosphides and is of the order of 0.5 wt.% Ni and 0.5 wt.% P. Measurements of Ni and P interface compositions from phosphides greater than 5 μm in size and from the adjoining kamacite-α are listed in Table 1. These inter-

### Table 1

<table>
<thead>
<tr>
<th>Globule No. in section A</th>
<th>Phosphide</th>
<th>α Phase</th>
<th>Equilibration temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni (wt.%)</td>
<td>P (wt.%)</td>
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</tr>
<tr>
<td>17</td>
<td>14.6</td>
<td>15.5</td>
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Fig. 3. (a) Widmanstätten pattern formed in globule No. 20, section A (refer to Fig. 2b). Small, dark oriented particles are phosphides. Field of view is 0.85 mm × 0.65 mm. (b) SEM photograph of one Widmanstätten plate in globule No. 20, section A. The kamacite-α boundary is decorated with micron-sized phosphides. Smaller phosphides are observed in the matrix. Field of view is 115 μm × 110 μm.
face compositions are consistent with the tie line compositions of α and phosphide in the Fe–Ni–P phase diagram at 600°C [5]. The lack of dendrites and the establishment of solid-state exsolution features which are in equilibrium to ~600°C argue for slower cooling than is normally observed for lunar spherules (>1°C per second) as discussed by Blau and Goldstein [6].

Silicate material of two distinct types was found adhering to the exterior surface of the “cluster”. The first and most widely distributed type is found as a layer up to 50 μm thick, which is preserved in shallow embayments in several locations where it is fused onto the metal. This type is composed of glass and fragments of anorthite-rich plagioclase. Since no thin sections were studied, it is not possible to discuss the shock status of the silicate material. Representative analyses of the glass and associated plagioclase were made and the calculated CIPW norm of the glasses show them to have the composition of noritic and troctolitic anorthosite. The compositions and relative amounts of glass and plagioclase are appropriate to their derivation from the regolith of the Apollo 16 site or any regolith overlying Highland type rocks.

The second type occurs as a single lens of material which is illustrated in Fig. 4. This material was friable and took a poor polish. It appears to be a crystalline rock made up of broken fragments of plagioclase, An95-98, with sporadic <5-μm inclusions of olivine or pyroxene and larger angular crystals of kamacite and troilite. It comes into contact with the outer edge of the metal cluster without fusion of the silicate at the contact. The composition of the metal in the silicate lens differs from the metal of the globule in having about 1% more nickel and a lower content of phosphorus, (<0.2%). The mineral association of this anorthositic fragment, like the first type, is of local or highland origin. The iron content of the plagioclase is greater than that in coarse-grained slowly cooled anorthosites, Fe 0.025–0.036 against ~0.010 cations per formula unit. This adhering fragment was probably derived from a recrystallized anorthite-rich regolith already containing some meteoritic kamacite. The crushed silicate-metal-troilite structure in the lens is accompanied by a local distortion and recrystallization (reheating) in the mass of metal which is in immediate contact with the crushed lens.

4. Discussion

4.1. Thermal history

Single globules of metal have been found in all the lunar soils [6]. They are thought to arise mainly from impact processes in which either projectiles or targets containing metal, sulfide and phosphide are remelted and/or vaporized. Individual metal globules or droplet are produced and each particle solidifies either in the vacuum by radiation cooling and/or within a lunar rock or soil by conduction processes at a rate of 1°C/s to 10^6°C/s [6]. Only a few of these spherules are remelted meteorite material, i.e., projectiles, which have impacted on the moon’s surface. Most of the single globules contain remnants of the solidification structure, i.e., dendrites, cellular-dendrites or rounded metallic areas. This paper reports the first occurrence
of a specimen where several hundred metal globules are all stuck together in a grape-like cluster. In this grape cluster particle the individual globules do not have a remnant solidification structure. Also phosphide-kamacite interface measurements from exsolution of phosphides indicate equilibration to 600°C.

According to the Fe–Ni–P phase diagram, the following sequence of transformations should occur for an Fe–Ni–P alloy of the same composition as the individual globules (6.25 wt.% Ni, 0.8 wt.% P, Fe) in the grape cluster particle. From the solidification temperature (~1300°C) to ~1100°C, the metal is one phase α (kamacite) with no interdendritic phosphide or sulfide. Below ~1100°C, the metal transforms to one phase γ (taenite). Insofar as the kinetics of the process are concerned, metallurgical experience is that cooling periods of a few days to a few weeks in the temperature range 1300–875°C will allow the removal of the previous solidification structure, the chemical homogenization of each globule and the formation of single crystals of γ below 1100°C. In this temperature interval the high-P eutectic-type material between the globules also solidifies and helps weld the final metal cluster into one mass.

Below 875°C the structure of the individual globules transforms to α (kamacite) by the reaction γ → α + γ. In this case the α may form via a Widmanstätten structure as often observed in iron meteorites [7]. At 700°C, if equilibrium is maintained, over half the structure will be γ phase. If no competing process occurs, the transformation to α (kamacite) should be completed at 600°C and each globule should be one single crystal of α. However, below about 700°C the solubility of P in α is exceeded and phosphide (Ph) should be expected to form by the reaction α + γ → α + γ + Ph. Nucleation of phosphide may occur initially at α/γ or α/α boundaries. This process may pin the α/α boundaries and preserve the Widmanstätten pattern formed at higher temperatures, as in particle No. 20 (Fig. 3a, b). In globules of other compositions (slightly lower P contents) the nucleation of phosphide may not take place until after the α phase has completely formed. The microstructures of several globules where little or no residual Widmanstätten pattern remains can be seen in Fig. 2a. No evidence of any residual γ phase has been found after detailed microprobe examination.

The Widmanstätten structures illustrated in Fig. 3a and b are approximately 3 orders of magnitude smaller than those of the transitional hexahedrite to octahedrite structures encountered in iron meteorites of the same nickel (6.25 wt.%) content. Cooling rates of iron meteorites of this transitional structure have not been determined because of the complexities introduced by the presence of large amounts of phosphorus (≥0.7 wt.%). The presence of phosphorus increases the nucleation temperature of the Widmanstätten pattern [7] with respect to the binary Fe–Ni diagram and makes the simple binary cooling rate models inoperative. Taking all uncertainties into consideration we estimate the cooling rates, during the formation of the Widmanstätten pattern in the globule particles in the temperature range 875–600°C, to be of the order of 1°C/hr to 1°C/day.

4.2. Hypothesis of formation

The source of the original metal is unknown. The bulk composition is similar to that found for iron meteorites at the coarsest octahedrite-granular hexahedrite type, but this does not prescribe its origin. The method by which several hundred globules, all of the same composition, are formed is difficult to explain. We must also explain how the globules could all adhere to each other without lunar silicate or fine soil being incorporated between them. The uniformity of composition suggests that all the metal globules must have come from one source. The globular form without crystal faces suggests that the globules are not a vapor condensate, that is formed by the reaction vapor → solid, and indicates that the material existed at one time as melted or partially melted spheroids. When the spheroids adhered to one another they must also have been partially solid. If not, the spheroids would simply have combined to form larger spheroids. The absence of silicate inclusions implies either that the source was essentially metallic or that some efficient separation process has operated during the accretional history of the cluster. At a later stage some minor silicate has impacted on the surface of the particle due to the process which finally excavated the composite cluster.

The composite cluster must have been quickly buried in a hot lunar regolith to allow for the relatively slow cooling (days to months) of the sample. Calculations of the cooling times of various thicknesses of lunar ejecta blankets [8] show that a depth of burial of 0.5–5 m is all that is necessary. Such a depth of burial
would introduce some small pressure due to the overburden which would aid in the process of globule sintering. Good evidence for high-temperature sintering during the cooling process is seen in Fig. 2b. However, the high temperature and pressure is not great enough to change the relatively loose original packing of the metal globules.

Two possible mechanisms, primary impact and secondary impact, can be proposed for the formation of the grape cluster particle. The first mechanism (primary impact) involves the impact of an iron meteorite on the surface of the lunar highlands. Very large numbers of molten metal "droplets" may be formed directly during impact or indirectly from the shock-produced metallic vapor phase. The compositions of individual molten metal spherules produced directly during impact may, however, vary depending on the structure and compositional heterogeneity of the impacting iron. If a meteorite has a coarse microstructure, such as the Canyon Diablo iron, with large phosphide and sulfide areas, the spherules produced by the shock process will vary in composition [9]. If the impacting meteorite has a more uniform structure, similar to that of a hexahedrite, the molten metal spherules may all be quite similar in composition. On the other hand, molten metal spherules condensed from a vapor phase, in which the metal may have homogenized chemically, will be quite similar in composition. If the molten spherules or globules produced directly or from the vapor phase adhere to one another above or on the lunar surface, a grape cluster particle can be formed.

During the same impact, melted and unmelted meteorite material will also be distributed along with very large quantities of shocked and melted highlands rock. There is a large probability that these materials may also be included in some way within the cluster as it is formed. However, if the molten metal spherules are ejected from the projectile as jets with specific directions and velocities, the grape cluster particle may form before it reaches the moon's surface. On the other hand, metal droplets condensed from the vapor phase may form a grape cluster particle as long as enough time is available before condensing silicate liquid may be incorporated. It is not possible to estimate the relative contributions of impact produced vapor or liquid phases.

The second mechanism (secondary impact) involves the production of the globules by splashing of metal from a liquid pool. During a major meteorite impact, the shock pressures may allow a local pool of iron metal to be produced on or near the surface of a hot ejecta blanket. The liquid pool of metal will only have a short lifetime before solidification because of its high liquidus temperature (1000–1400°C, depending on the P content) which favors crystallization and its high density which favors the draining away of the metallic liquid. If the metal pool persisted long enough a secondary projectile from the fall back could produce a localized coherent spray of metal globules uncontaminated by silicates. Each spherule will have a very similar composition since it comes from a chemically homogeneous source liquid. Some of these partially solidified spherules become attached to form the fragile grape cluster. Little or no shocked and melted highlands rock is expected to be formed according to this mechanism.

An analogous splashed-liquid or lava lake impact origin for the Apollo 17 "orange soil" has been suggested [10]. However, the production of this type of glass may occur either by impact or volcanic routes. Heiken et al. [11] have made a detailed investigation of the several hypotheses that are available to explain the formation of lunar orange soils. They favor a lava fountain hypothesis (volcanic route) over the lava lake impact hypothesis. We cannot invoke the lava fountain mechanism for the grape cluster particle because the amount of metal normally found in silicate liquids is small and metal is usually produced by reduction processes from the solidifying silicate liquid [12,13]. Both the primary and secondary impact mechanisms call for very specific conditions and sequences of events in order to produce the grape cluster particle. It is not surprising therefore that the occurrence of such a particle is rather unique. It appears that either mechanism could produce the grape cluster particle. Both mechanisms argue for the origin of the grape cluster particle from an impacting iron meteorite.

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References

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