

**THE STRUCTURE OF REFRACTORY METAL ALLOYS, CONDENSATES FROM THE EARLY SOLAR NEBULA.** D. Harries<sup>1</sup>, T. Berg<sup>2</sup>, H. Palme<sup>3</sup>, and F. Langenhorst<sup>1</sup>, <sup>1</sup>Bayerisches Geoinstitut, Universität Bayreuth, 95440 Bayreuth, Germany (dennis.harries@uni-bayreuth.de), <sup>2</sup>Institut für Physik, Johannes Gutenberg-Universität Mainz, Staudingerweg 7, 55128 Mainz, Germany, <sup>3</sup>Forschungsinstitut und Naturmuseum Senckenberg, Senckenberganlage 25, 60325 Frankfurt am Main, Germany.

**Introduction:** Recently, [1] described submicrometer refractory metal nuggets (RMN) with compositions matching predicted nebular condensates. The nuggets were recovered from acid resistant residues of the Murchison meteorite and may have originally resided in Ca,Al-rich inclusions. The particles contain high but variable concentrations of Os, Ir, Mo, Ru, and Pt with subordinate amounts of W, Rh, Ni, and Fe. The presence of major amounts of Mo (up to 40 wt%) and some W in the alloy distinguishes these particles from any known terrestrial noble metal alloy or compound and excludes major oxidation during retrieval of the nuggets. The only common feature of the elements in the alloy is their low vapor pressure. Any metal with a vapor pressure below that of metallic Fe is completely absent, e.g., Au and Pd. Comparison of the compositions of the nuggets with those expected from thermodynamic condensation calculations suggests that these particles formed by condensation of refractory metal alloys in a nebular environment within a temperature range from 1600 to 1400 K at an assumed pressure of  $10^{-4}$  bar [1].

The morphology of the particles suggested dissolution of all metals in a single alloy, despite differences in the crystal structures of the pure individual metals: hexagonal close-packed (hcp) for Os and Ru, cubic close-packed/face-centered cubic (fcc) for Ir, Ni, Pt, Rh, and body-centered cubic (bcc) for Mo, W, and Fe (also fcc). [2] predicted condensation of refractory metal alloys into three different crystal structures, as hcp alloys of Ru and Os, bcc alloys of Mo and W, and as fcc alloys with Ir, Fe, Ni. Later mixing produced the observed opaque assemblages (OA) or Fremdlinge in CAIs. [3] favored condensation into a single refractory metal alloy. These predictions were based on the observation of micrometer sized OA, which contain oxidized, sulfurized and exsolved phases of original metal condensates. In these assemblages Mo occurs as molybdenite, W as scheelite, Os and Ru as hcp alloy and FeNi with Pt and Ir. The population of the submicrometer sized particles studied here escaped oxidation and sulfurization and has presumably retained its original structure and composition.

Here we report the results of a transmission electron microscopy (TEM) study including quantitative analyses of the submicrometer sized particles to answer the following questions: What are the crystal structures of the RMNs? Are they single alloys or mix-

tures of several different alloys? Are the nuggets compositionally uniform or are they zoned?

**Methods:** We used the focused ion beam (FIB) technique to sample 15 compositionally diverse RMNs from the SiC-rich, acid resistant residue previously studied by [1]. We specifically focused on including chemically diverse grains into our selection for TEM preparation in order to search for structural variations.

The sampled RMNs range in size from 200 to 900 nm and show isometric (almost spherical) to rarely platy morphologies. In order to securely fixate particles on the graphite substrate and aid targeting in the ion beam image, selected grains were covered with platinum by electron beam deposition (at 5 keV) prior to FIB processing. This approach also preserves external grain surfaces free of ion beam damage. After in-situ lift out and attachment to copper grids final thinning to electron transparency was done with lowered beam currents down to 10 pA at 30 keV energy. Final thicknesses were in the range of approximately 60 to 80 nm and sufficient to record clear selected area electron diffraction (SAED) patterns from these highly dense materials.

**Results:** We have found that all 15 grains studied are monophasic single crystals. The electron diffraction patterns of all grains can be unequivocally indexed in terms of a hcp metal structure (space group  $P6_3/mmc$ ). This includes also all those grains, which are compositionally dominated by metals that are non-hcp structured at ambient conditions, such as Mo and Ir (amounting to ~60 to 67 at%). The diffraction patterns show no evidence for exsolution, compositional modulation (e.g., spinodal decomposition leading to diffuse satellite reflections) or superstructure formation. Preliminary results of EDX spectroscopy in scanning TEM mode at high spatial resolution (< 10 nm) indicate the absence of compositional zoning across individual grains, except for small Fe (and likely Ni) deficits at the outermost margins of some grains (less than 20 nm from the surface). Because the depletion is limited to Fe and Ni and confined to the outermost margins of the otherwise uniformly composed grains, these observations likely represent artifacts of the measurement (decreased X-ray self-absorption at the grain edge) or sample preparation (oxidation and acid leaching of Fe) rather than to truly primary features.

Observed microstructures within individual RMN grains are scarce. As indicated by clearly defined dif-

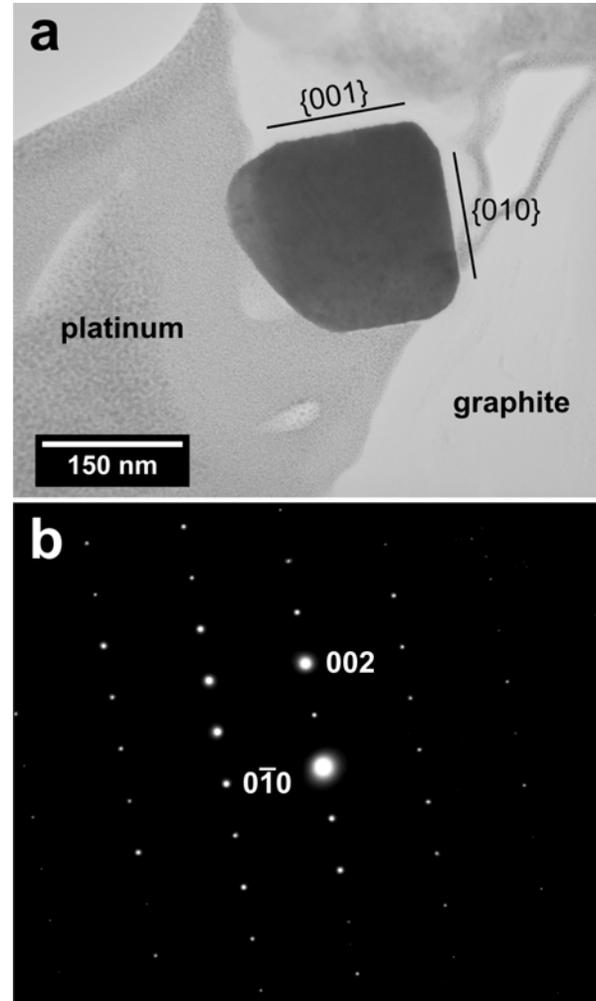
fraction patterns the grains are well crystalline with few defects.

Our findings of solely hexagonal metal alloys are in accord with TEM observations by [4] on five RMNs hosted in spinel of fluffy type-A Allende CAIs. Also in these grains no internal compositional heterogeneity was detectable. The Mo-dominant grains of our study match the structure and approximate lattice parameters of the hexamolybdenum phase described by [5] from an Allende CAI, where it occurs in association with Sc,Zr-rich ultrarefractory oxides, perovskite, and Os-rich alloys. Particularly interesting is that the hexagonal structure in their sample appears to be preserved even for compositions with just about 20 at% hcp metals (Ru+Os).

**Discussion:** No experimental data exists on the phase relation in the quaternary system Mo-Ru-Os-Ir and phase diagrams on intermetallic systems are generally completely absent for low pressures. However, the Mo-Ru binary system for 1 atm clearly shows a fairly wide miscibility gap between bcc and hcp solid solutions at temperatures below 1600 K. Furthermore, the system contains an intermetallic compound ( $\sim\text{Mo}_5\text{Ru}_3$ ) at temperatures between 1416 and 2188 K [6]. Also, the Ir-Os and Ir-Ru binary systems for 1 atm show (comparatively smaller) miscibility gaps between fcc and hcp alloys at temperatures below 2000 K [7,8]. Consequently, based on the 1 atm phase diagrams one would expect to find structural diversity among Mo-Ru-Os-Ir alloys having additional significant contributions of Pt, W, and Fe. The observed absence of such diversity despite highly variable compositions might have several reasons:

Firstly, the nucleation of hcp structured Mo-Ru-Os-Ir alloys might be favored by the low formation pressures in the solar nebula. Secondly, the homogeneity region of a hcp solid solution in the 4+n component system might be much larger than expected from simply extrapolating the binary solvi (limiting the hcp solid solution fields) of the major components. Or thirdly, the observed alloys might be preserved in a metastable structural state, possibly due to combination of preferred primary hcp nucleation (Os-rich as predicted by [1]) and hindered nucleation of exsolving phases. However, the lack of zoning within RMNs and the variations among them points to good equilibration between RMNs and their growth medium at given temperatures when material exchange was possible (i.e., before enclosure into other phases). If sufficient activation energy was available to drive diffusive equilibration then one might expect that also overstepping the nucleation barrier of exsolution was possible (given that the bulk composition lies far enough into a two-phase field).

In either case, the internally homogeneous but otherwise highly variable RMN grain compositions and consistently hexagonal crystal structures clearly support a single phase condensation of these early indigenous solid materials of the solar system.



**Figure 1:** a) BF-TEM image of the smallest sectioned RMN. The presence of crystal faces is evident. b) Corresponding SAED pattern of the same grain and orientation, indexed for the hexagonal zone axis [100]. Indexing in the cubic system is not possible. Assignment of crystal forms in a) is based on this pattern.

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