Journal of Crystal Growth 429 (2015) 63–67

Contents lists available at ScienceDirect

Journal of Crystal Growth

journal homepage: www.elsevier.com/locate/jcrysgro

The low temperature electrochemical growth of iron, nickel and other metallic single crystals from halide eutectic fluxes in a temperature gradient

Dmitriy A. Chareev *

Institute of Experimental Mineralogy, Russian Academy of Sciences, Chernogolovka, Moscow District 142432, Russia

ARTICLE INFO

Article history:
Received 13 April 2015
Received in revised form
24 July 2015
Accepted 31 July 2015
Available online 28 August 2015

Keywords:
A1. Dendrites
A1. Recrystallization
A1. Solid solutions
A2. Electrochemical growth
A2. Growth from solutions

ABSTRACT

Single crystals of metallic Fe, Ni, Co, Cr, Al, Cu, Ag, Au, Pd, Pt and a few alloys were grown using the $AlCl_3$/KCl and CsCl/NaCl/KCl fluxes for Me^{n+} transport and an inert metallic wire for electron transport in a permanent temperature gradient from 350–600 °C that produced single crystalline samples with dimensions of approximately $2 \times 2 \times 2$ mm^3. Energy dispersive X-ray spectroscopy established crystal formation of pure metals.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

It is well known that the single-crystalline state is useful for studying the anisotropic properties of solids. Moreover, decreasing the surface area reduces the surface contribution to the general properties of the crystal and increases its chemical stability. Often the use of a substance in the single-crystalline state automatically leads to the elimination of additional phases (heterogenic impurities).

Basic techniques for metal crystal synthesis are based on crystallization from the melt of the corresponding metal. Nevertheless, crystal synthesis at temperatures significantly below the melting point is preferable because first, the lower temperature reduces the number of equilibrium defects, and second, when cooling from relatively low temperatures, the substance may not go through high temperature phase transitions that destroy the integrity of the crystal. For example, the synthesis of single crystalline iron at temperatures below 917 °C avoids destruction during the two-phase transitions of BCC–FCC and FCC–BCC. At low temperatures, metal single crystals can be obtained primarily using the gas transport [1] or solution-melt techniques [2], which are based on cooling a melt of complex composition, leading to its partial crystallization. Crystals, whiskers and films of metals, alloys and intermetallics at low temperatures can be electroformed [3]. Water solutions and molten salts can be used as nutrient media for electrochemical growth. For example, in the study [4], molten alkali metal chlorides that contained an amount of the metal chloride, which was supposed to be electrochemically reduced, were utilized.

Growth of metal crystals, alloys and intermetallics using the gas transport technique began as early as the 19th century. For example, Meunier [5] grew the needles of iron–nickel alloys by decomposing iron and nickel chlorides with hydrogen.

In 1893, Liversidge obtained gold dendrites [6] by storing gold foil for several weeks in a solution containing gold chloride, sodium chloride and various oxides and salts of other metals capable of reducing gold.

Additionally, millimeter sized crystals of many metals (Au, Pt, Sb, Ni, Co, Te, As, Ag, Ta, and Ge) have been grown hydrothermally [7]. The synthesis was conducted in quartz ampoules in concentrated solutions of HCl, HBr or HI. The growth was performed in a temperature gradient; the temperature of the hot end was 420–600 °C. To prevent the ampoules from bursting, they were placed in autoclaves with dry carbon dioxide, which created counterpressure during vaporization. Addition of an oxidizer to the solution, for example, Cl_2, Br_2, H_2O_2 or remaining oxygen, has also been shown to sharply increase metal transport due to the increased concentration of metal ions dissolved in water.

* Tel.: +7 910 463 89 23.
E-mail address: chareev@iem.ac.ru

http://dx.doi.org/10.1016/j.jcrysgro.2015.07.038
0022-0248/© 2015 Elsevier B.V. All rights reserved.

2. Halide eutectic flux technique

A very low melting eutectic molten salt mixture ($AlCl_3$/KCl) has been used to synthesize single crystals of superconducting $FeSe_{1-\delta}$ in a permanent temperature gradient [8] at temperatures well below the melting point of the Fe–Se system. The crystals were formed after the starting chemicals located at the hot end of the reaction vessel at 427 °C gradually dissolved in the molten salt and were transported to and crystalized at the cold end, the temperature of which was ~50 °C lower. Iron and selenium were transported through the molten salt as positively and negatively charged ions, respectively. An attempt to grow iron crystals in a similar manner failed because electrons must be removed to convert the metal into the dissolved ionized form and added to the cold end of the ampoule at the area of the metal crystal growth. Electron migration directly through the molten salt (electrolyte) is impossible, but electrons can migrate from the load to the cold end through wires composed of a sufficiently inert material, e.g., platinum (Fig. 1). The inert wire can be replaced by a wire composed of the metal whose crystals are being grown.

Thus, the process of metal crystal growth in molten salts can be described by two electrochemical reactions. At the hot end, the initial metal powder (the source of the metal) is dissolved and the electrons are released, as follows:

$$Me_{powder} = Me^{n+}_{liq} + ne_{wire}\ (\text{hot end},\ \text{anode})$$

The electrons migrate through the wire to the cold end, recombine with the ions and form the metal crystal, as follows:

$$Me^{n+}_{liq} + ne_{wire} = Me_{crystal}\ (\text{cold end},\ \text{cathode}).$$

Platinum wire can be insulated from the molten salt because the metal ions and the electrons migrating to the cold end can form a reduced metal along the length of the bare platinum wire. Such local dynamic equilibriums cannot eliminate the moving force that causes transport, but they will likely decrease the metal migration rate. Additionally, the interaction of the metal being transported with the platinum wire can result in nonconvertible formation of solid solutions that will reduce the metal transport rate to the cold end of the ampoule even further. The wire can be separated from the molten salt by a quartz glass capillary (Fig. 1).

When considering the processes of electrochemical crystal growth, one should always take into account the condition of electroneutrality. Therefore, dissolution of the load at the hot end and metal crystallization at the cold end likely need to occur simultaneously. For this purpose, the melt should initially have a nonzero concentration of metal ions that are to be transported. This can be achieved by adding several milligrams of the corresponding metal halide or elemental iodine to the molten salt. Additionally, one can hope for minor oxidation and dissolution of the metal from the load due to reduction and transition to the solid state of the alkali metals from the salt eutectic.

Metal crystals can be grown not only using powdered starting chemicals and an inert (platinum) conducting wire, but a wire composed of a similar metal that can serve as a conductor and as the initial material (the source of metal) can also be used.

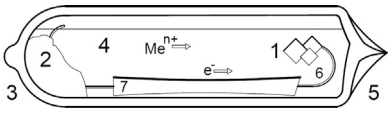

Fig. 1. Design of quartz ampoule for metal single crystals growth: The metal single crystals. (1) The load, (2) the hot end of the ampoule, (3) The halide eutectic flux, (4) the cold end of the ampoule, (5) the conducting wire, and (6) the quartz capillary.

Thus, a necessary condition for metal crystal growth in molten salts in permanent temperature gradients is the presence of an inert electron conductor. Additionally, the growth must first be facilitated by insulating the conducting wire from the molten salt and then by adding the dissolved metal to the molten salt.

To prove such a mechanism, metal transport in the absence of a conducting wire should be studied.

At present, molten metal halides (mostly alkali metals and aluminum chlorides) are mainly used to synthesize single crystal halides [9]. Most crystals are obtained by slowly cooling the molten salt that is saturated with the components of the crystal [10]. An alternative to this technique is growing crystals in permanent temperature gradient [8]. Metal crystals cannot be grown using the slow cooling technique because there is no potential for charge transfer during crystallization.

A common disadvantage of all variants of molten salt synthesis is the possibility of the salt eutectic components dissolving in the growing crystal.

The analysis of various binary diagrams [11] has shown that the solubility of alkali metals (cesium, sodium and potassium) and chlorine in iron is practically zero. At temperatures below 550 °C, as much as 20 at% of aluminum can dissolve in iron. Iron crystals obtained in aluminum chloride-based eutectic should not contain this much aluminum because the activity of aluminum in eutectic melts of chlorides is lower than in metallic aluminum coexisting with iron.

Binary phase diagrams containing most metals reveal extremely low solubility of cesium, sodium and potassium. Phase relations of metals and chlorine are practically unknown, but zero chlorine solubility in metals is also expected. In contrast, the solubility of aluminum is high and sometimes reaches 20%.

Thus, most metal growth experiments have been conducted in eutectic molten salts based on alkali metal chlorides, and only several in experiments have been performed on aluminum chloride-based melts.

3. Experimental section

The metal single crystals were grown in evacuated quartz ampoules using a chloride flux [9] and a permanent temperature gradient [8].

The starting chemicals were potassium, sodium, cesium chlorides (KCl, NaCl, and CsCl), anhydrous aluminum chloride ($AlCl_3$) (Fluka, 98%) and metal pieces, wires or powders.

Additionally, wires of various thicknesses composed of stainless steel, FeCrAl alloys, constantan, nichrome, palladium and platinum were used.

The metals were loaded into a silica ampoule with a length of 110 mm. Then, the wire was placed along the entire length of the ampoule so that one end of the wire was in contact with the metals and the other end was fully submerged in the molten salt as close as possible to the opposite end of the ampoule. In some cases, the wire was placed inside a quartz capillary with its ends remaining bare. Next, the eutectic mixture of salts was placed in the ampoule. For synthesis in the 550–600 °C temperature range, the CsCl/KCl/NaCl mixture was used in the ratio of 68/17/15 wt%, for synthesis in the 350–450 °C range, $AlCl_3$/KCl was used in the ratio of 78/22 wt%. For some experiments, several milligrams of crystal iodine were added to the salt mixture. The ampoule was evacuated to 10^{-4} bar pressure and sealed. The experiments performed with hygroscopic $AlCl_3$ have been described with more details in the literature [8].

The ampoule was loaded into a horizontal tube furnace, heated to the desired temperature for synthesis for 3–4 h, and then maintained at this temperature for 20–50 days. The temperature

Download English Version:

https://daneshyari.com/en/article/1789961

Download Persian Version:

https://daneshyari.com/article/1789961

Daneshyari.com