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Non-equilibrium solid solution of molybdenum and sodium: Atomic scale experimental and first principles studies



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ABSTRACT

We report a combined experimental and first principles study of an extremely immiscible alloy of Mo with 1 and 2 at.% Na, which was produced by high-energy ball milling. The microstructure of the asmilled and annealed state were examined by various methods, including atom-probe tomography (APT), transmission electron microscopy, and energy-dispersive (EDX) analysis. Despite the complete immiscibility of the Mo-Na system in the solid and even in the liquid state, APT measurements clearly evidence the formation of a true nanocrystalline solid-solution microstructure with insignificant Na clustering for samples with 1 at.% Na. In agreement with our x-ray diffraction experiments, first principles calculations expose that the Na atoms do not expand the Mo lattice, which is in contrast to predictions using Vegard's rule. Heating at 700 °C induces only slight grain growth while the solid solution segregations at triple junctions and significant grain growth are observable, although the solid solution still retains most of the dissolved Na.

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1. Introduction

The search for novel materials with outstanding properties is of high technological and fundamental relevance. With this regard it is beneficial to take also unconventional element combinations, non-equilibrium states as well as alloys consisting of immiscible elements, into account. The equilibrium solubility of alloying elements in solid solution depends on their atomic size difference, valency, electronegativity, and crystal structure [1]. These properties should be preferably similar to achieve a low enthalpy of mixing and, therefore, a high solubility. On the contrary, combinations of elements with strong positive enthalpies of mixing usually exhibit nearly no solubility and are not considered as proper "technical alloys" at least at first sight. The aim of the present work is to demonstrate that alloying of such completely immiscible "non-alloy" systems with extremely high enthalpy of mixing by use of high-energy ball milling is feasible as well as to understand the thermal stability of such extremely non-equilibrium alloy systems. For this study the system Mo-Na was chosen as model system.

Mechanical alloying is of great scientific importance due to its capability to create different crystalline and amorphous alloyed microstructures unattainable by any other technology from the liquid state, such as casting or rapid solidification techniques [2] [3]. During the last decades extended solubility was achieved in systems with minor solubility at room temperature by use of high-energy ball milling in some amorphous [4,5] or crystalline binary systems [6,7,8,9,10,11,12,13] as well as by high-pressure torsion [14]. However, all those crystalline alloys reveal an at least small solubility (smallest: Ag in Fe of 0.02 at.% [15]) and, in particular, complete solubility in the liquid state at high temperatures. The latter implies the feasibility of rapid cooling techniques to produce alloys. However, systems with no common liquid phase, i.e. where melting techniques are not applicable, and with no solubility in the solid state have not been investigated so far.

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between balls during their collisions. Thereby, the particles become strongly plastically deformed leading to work hardening and particle fracture. Within the continuous milling process the particles become constantly flattened, fractured and welded, and, furthermore, the alloying elements become homogeneously distributed [2,3]. Plastic deformation introduces crystal defects such as dislocations and vacancies leading to an increased diffusivity of the solute atoms [16]. Additionally, due to the resulting fine-grained microstructure the diffusion distances are reduced. The therefore improved diffusion amongst the elements leads to the actual alloyed state [2]. For immiscible systems with a positive enthalpy of mixing, the increasing dislocation density, the lattice strain and the small grain size as a consequence of milling also play an important role to achieve solubility [16,12,17]. In particular, the large number of dislocations act as diffusion channels for solute atoms [11]. Throughout milling these dislocations are moving within the crystals as a consequence of the exerted forces of the balls on the material. It has been proposed that during dislocation movement solute atoms inside the core of dislocation could be depinned and left behind in solid solution [18]. In this regard, strain-induced atom mixing has been discussed as a further possible mixing mechanism in recent years [19]. For instance, Guo et al. [20] showed for alloys of Cu and Zr that dislocations could drag solute interstitial atoms and move them from one phase into another.

Amongst the immiscible systems a binary alloy consisting of Na and Mo represents an extreme case because of their large differences in melting and boiling temperature. For Na the melting (97.72 °C) and boiling point (890 °C) are much lower than the melting point of Mo (2623 °C). As a consequence, no liquid phase alloying process is applicable to synthesize an alloy within this system [21]. Other physical properties of pure Mo and Na also differ quite remarkably. In particular, their atomic-size difference [1], exceeding 24%, and their lattice mismatch of 36% [22,23] are supposed to be an obstacle for the alloying process taking into account the Hume-Rothery rules [1]. Moreover, the elastic constants of both metals differ by more than one order of magnitude (e.g. the shear modulus of Mo is about 40 times larger than that of Na [1]). Because of such property differences alloying could be greatly inhibited [2], and, in addition, the formation of a solid solution could be hampered [24].

So far, the introduction of Na atoms into the Mo lattice was only achieved by use of ion implantation and subsequent annealing procedures [25,26]. However, no solid solution could be obtained. Instead, immediately after the implantation Na formed precipitates at the locations of maximum radiation damage, most probably due to the high Na concentration of up to 8 at.%.

Here, the Mo-Na alloy was produced by mechanical alloying utilizing high-energy ball milling. The formation of the alloy and the thermal stability are studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atom probe tomography (APT). Furthermore, the subsequent modifications of the crystallographic and electronic structure arising after alloying are important issues of this article and are examined by use of a combination of X-ray powder diffraction (XRD) and first principles calculations.

2. Methods

High-purity Mo powder delivered by the company H.C. Stark with an average particle size of (d_{50}) 16 μ m and Na pieces from Alfa Aesar (purity 99.95%) were utilized as base material for mechanical alloying. Both materials were weighed to obtain the target fraction of 1 and 2 at.% Na. Before milling, the Mo powder has been annealed in hydrogen atmosphere at 900 °C for 1 h to reduce the oxygen content of the powder. For milling we applied a Retsch MM 200

mill. Both the sample preparation and the milling was carried out inside an argon glove box to avoid the uptake of oxygen and nitrogen. The milling was performed with a ball to powder ratio of 33g/4 g and a frequency of 25 Hz, the milling container and the milling balls are made of stainless steel. The maximum milling time amounted to 75 h. To investigate the alloying progress samples of the milled powder have been taken each 15 h.

A fraction of the powder was annealed in a tube furnace under argon atmosphere. The samples were heated up with a rate of 10 K/min to a target temperature, which was kept constant for 1 or 5 h, and afterwards cooled down inside the furnace.

SEM images were recorded using a Zeiss DSM 982 GEMINI microscope with an integrated Noran Voyager 2000 system for energy-dispersive x-ray analysis (EDX) applied for quantitative element analysis.

XRD patterns were detected using a Brucker D8 Discover spectrometer with Cu-K α radiation and a Vantec 2000 two-dimensional detector. The reflected spectrum was measured at six detector positions to cover 2θ -values from 8 to 125° . The obtained detector signal was integrated, the different spectrum parts were merged and, finally, a polynomial background signal was subtracted.

The microstructure of some samples was studied by analytical TEM. Due to the small size of the powder particles of a few μ m the samples were prepared using the lift-out technique in a focused ion beam (FIB) facility [27]. A Helios 660 device from the company FEI, equipped with an "Easylift" micromanipulator, was utilized to extract a representative slice. TEM analysis was executed in a Libra 200 MC CsSTEM from Carl Zeiss, operating in the bright-field STEM mode in combination with an Oxford Inca EDX-system, which allows local elemental analysis on the nanometer scale [28].

APT specimens were prepared using a dual-beam FIB system (FEI Helios Nanolab 600i) employing the lift-out procedure described in Ref. [29]. To reduce Ga implantation, a 2 keV Ga beam was used for the final polishing. Consequently, the residual Ga contamination did not exceed 0.25 at. %. APT analyses were performed by a reflectron-equipped local electrode atom probe tool (LEAP 4000X HR, Cameca Instruments) in the laser mode. Laser pulses of 355 nm wavelength, 12 ps pulse length, 10–70 pJ pulse energy, and 250 kHz frequency were applied, while the specimen base temperature was kept at about 60 K. Data reconstruction and analysis were carried out using the Cameca IVAS 3.6.8 software package. Reconstruction parameters (evaporation field and imagecompression factor) were adjusted to obtain the final reconstruction radius as well as the length of analyzed volume matching to SEM images of a specimen before and after an interrupted APT measurement.

First principles calculations within the framework of density functional theory [30,31] (DFT, as implemented in the Vienna Abinitio Simulation Package (VASP)) [32,33] were performed. Reciprocal space corresponding to a conventional body-centered cubic (bcc) cell, containing 2 atoms, was sampled with $16 \times 16 \times 16$ kpoints. According to our convergence tests, the chosen k-mesh together with the employed plane-wave cut-off energy of 600 eV and projector-augmented wave method capable pseudopotentials [34] guarantee total energy accuracy in the order of 1 meV/atom. Specifically, we used pseudopotentials with valence configuration of 4p⁶5s²4d⁴ and 2p⁶3s¹ for Mo and Na, respectively. The quantum mechanical electron-electron interactions were treated within the generalized gradient approximation as parametrized by Wang and Perdew [35]. After optimizing the lattice parameter of bcc-Mo (a = 0.3172 nm), a $3 \times 3 \times 3$ supercell (54 atoms) was created for evaluating the impact of Na in Mo. In order to mimic the dilute limit, only the internal atomic positions were relaxed, while the shape and volume of the supercell was fixed.

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