RETRACTED: Manufacturing of Conductive, Wear-Resistant Nanoreinforced Cu-Ti Alloys Using Partially Oxidized Electrolytic Copper Powder

Stepan Vorotilo 1,*, Pavel Alexandrovich Loginov 1,*, Alexandr Yuryevich Churyumov 2,*, Alexey Sergeevich Prosviryakov 2,*, Marina Yakovlevna Bychkova 1,*, Sergey Ivanovich Rupasov 1,*, Anton Sergeevich Orekhov 3,*, Philipp Vladimirovich Kiryukhantsev-Korneev 1,*, and Evgeny Alexandrovich Levashov 1,*

1 Scientific-Educational Center of SHS, National University of Science and Technology “MISIS”, Leninsky Prospect 4, 119049 Moscow, Russia; pavel.loginov.misis@list.ru (P.A.L.); bychkova@shs.misis.ru (M.Y.B.; vosapur@mail.ru (S.I.R.); kiruhancev-korneev@yandex.ru (P.V.K.-K.); levashov@shs.misis.ru (E.A.L.)
2 Department of Physical Metallurgy of Non-ferrous Metals, National University of Science and Technology “MISIS”, Leninsky Prospect 4, 119049 Moscow, Russia; churyumov@misis.ru (A.Y.C.); pro.alex@mail.ru (A.S.P.)
3 Laboratory of Electron Diffraction, Federal Scientific Research Centre “Crystallography and Photonics”, Russian Academy of Sciences, Leninsky Prospect 59, 119333 Moscow, Russia; orekhov.anton@gmail.com
* Correspondence: s.vorotilo@misis.ru

Received: 25 April 2020; Accepted: 18 June 2020; Published: 28 June 2020; Retracted: 7 August 2024

Abstract: Reactive powder composites Cu-(0–15%)TiH$_2$ containing up to 5% native Cu$_2$O were manufactured by high energy ball milling and then hot-pressed to produce bulk nanostructured copper–matrix alloys reinforced by Cu$_3$Ti$_3$O inclusions. Two high-energy ball-milling (HEBM) protocols were employed for the fabrication of Cu-Ti alloys: single-stage and two-stage ball milling, resulting in an order of magnitude refinement of TiH$_2$ particles in the reactive mixtures. Single-stage HEBM processing led to the partial retention of Ti in the microstructure of hot-pressed specimens as the α-Ti phase and formation of fine-grained (100–200 nm) copper matrix interspersed with 5–20 nm Cu$_3$Ti$_3$O precipitates, whereas the two-stage HEBM led to the complete conversion of TiH$_2$ into the Cu$_3$Ti$_3$O phase during the hot pressing but produced a coarser copper matrix (1–2 µm) with 0.1–0.2 µm wide polycrystalline Cu$_3$Ti$_3$O layers on the boundaries of Cu grains. The alloy produced using single-stage HEBM was characterized by the highest strength (up to 950 MPa) and electrical conductivity ($2.6 \times 10^7$ Sm/m) as well as the lowest specific wear rate ($1.1 \times 10^{-5}$ mm$^3$/N/m). The tribological performance of the alloy was enhanced by the formation of Cu$_3$Ti$_3$O microfibers in the wear debris, which reduced the friction coefficient against the Al$_2$O$_3$ counter-body. The potential applications of the developed alloys are briefly discussed.

Keywords: metal–matrix composites; copper–titanium alloys; conductivity; connectors; Cu$_3$Ti$_3$O; HEBM

1. Introduction

Age-hardenable Cu-Ti alloys, which contain 3–5 mol.% Ti, have gained considerable attention for use in electrical devices such as microconnectors and relay controls because of their excellent mechanical strength, stress-relaxation behavior, stiffness, and good electrical conductivity [1–6]. These strong and highly conductive precipitation-hardened alloys are anticipated to become increasingly technologically significant as they replace the current state-of-art Cu-Be alloys in numerous applications. An unfortunate drawback of Cu-Ti alloys is their higher electrical resistivity as compared to Cu-Be,
induced by dissolute Ti in Cu matrix [1,6–8]. The aging of Cu-Ti leads to a trade-off between the electrical conductivity and mechanical properties. To improve the conductivity of Cu-Ti alloys without degradation of mechanical strength, Semboshi, et al. [6,9–12] developed a protocol for aging the Cu-Ti alloys in hydrogen \((T = 773 \text{ K}, P = 0.37 \text{ MPa}, \text{duration up to 180 h})\). This aging resulted in the permeation of hydrogen into Cu-Ti solid solution and binding of dissolved Ti, resulting in precipitation of titanium hydride \((\text{TiH}_2)\) from the copper matrix along with the main strengthening phase \(\text{Cu}_4\text{Ti}\). However, the required aging duration resulted in the coarsening of the alloys’ microstructure and degradation of mechanical properties [10–13].

The mechanical and conductive properties of Cu-Ti alloys can be simultaneously bolstered using the recently developed hierarchical reinforcement approach [14–18]. The hierarchical reinforcement can be achieved via the controlled condition-specific precipitation of primary and secondary phases at the micro- and nanoscale. The hierarchy of length scales is associated with a spatiotemporal (i.e., the spectrum of characteristic relaxation times) [14,19].

The design of hierarchically-structured structures relies heavily on the control of primary and secondary precipitation mechanisms. In particular, high energy ball milling (HEBM) treatment was instrumental in the formation of hierarchical structures in ceramics [20–23].

Recently, an in situ hydrogenation–reoxidation approach was developed for the manufacturing of conductive and strong hierarchically structured Cu-Ti alloys from commercially feasible Cu powders with 5% native \(\text{Cu}_2\text{O}\) [24]. The reinforcement was achieved via the segregation of Ti and O from Cu matrix and coherent precipitation of cubic \(\text{Cu}_3\text{Ti}_3\text{O}\) inclusions (TibNi-type structure stabilized by O) during hot pressing. Enhanced stiffness of the developed Cu-Ti alloy makes it a promising candidate for sliding electrical contacts and diamond binders [25]. Previously, a considerable enhancement of tribological performance of copper was achieved using Cu-Ti coatings [26] as well as by engineering of Cu-Ti-C [27] and Cu-Ti-Sn-C [28] nanocomposites.

This works aims to ascertain the influence of processing parameters on structure formation, mechanical properties, electrical conductivity, and tribological performance of hierarchically structured Cu-Ti alloys.

2. Materials and Methods

In this study, electrolytic copper powder (PMS-1 grade, Joint stock company “Uralelectromed”, Verkhnyaya Pyshma, Russia; Figure 1) with an average grain size of 40 \(\mu\text{m}\) and \(\text{TiH}_2\) powder, produced by hydrogenation of a titanium sponge, with an average grain size of 12 \(\mu\text{m}\), were used as initial materials. The concentration of \(\text{TiH}_2\) was varied in the range of 0–15 mass %. Copper powders contained 5% native \(\text{Cu}_2\text{O}\) [24], distributed on the surface of copper dendrites (Figure 1). The content of oxygen in copper powder measured by energy dispersive X-ray spectroscopy (EDS) was 1.8 wt.%.

**Figure 1.** The microstructure of the used copper powders obtained via scanning electron microscopy (SEM) (a) and transmission electron microscopy (TEM) (b); EDS maps of copper (c) and oxygen (d) in the copper powders.
2.1. Preparation of Reactive Composite Powders

The pure copper and Cu-1.15% TiH₂ powder mixtures were processed in high energy planetary ball mill Activator-2s with external water cooling (Activator Engineering Plant, Ltd., Novosibirsk, Russia) using the following regime: rotation speed 700 rpm, mass of milling media to powder mass—15:1. Isopropyl alcohol (10 wt.%) was added into the powder mixture to prevent the sticking of copper on milling media and the walls of the jars. The jars were filled with argon to prevent the oxidation of the mixture during the milling. The milling-associated pollution of reactive mixtures was below 1.5 wt.%, as measured by EDS.

Two milling protocols were employed: (1) single-stage HEBM of the mixture of Cu and TiH₂ powders during 10 min and (2) two-stage HEBM—first the TiH₂ powder was milled for 30 s, then the mixture of Cu and TiH₂ powders was milled for 10 min. The size of the resulting TiH₂ powders was determined via laser diffraction analysis using a Fritsch Analysette 22 Microtec Plus Instrument (Fritsch GmbH, Idar-Oberstein, Germany).

2.2. Hot Pressing of Reactive Composites

The compact samples were produced using the hot pressing technique (HP) in the vacuum on a setup DSP 515-SA (Dr. Fritsch GmbH & Co. KG, Fellbach, Germany). The maximum hot pressing temperature was 850 °C; 350 kg/cm² pressure at the maximum temperature; exposure duration 3 min (Figure 2). The temperature at which pressure started to be applied was determined according to the previously obtained results of the differential scanning calorimetry (DSC) of powder mixtures and corresponded to the end of TiH₂ decomposition [24]. The produced compact samples were cut for testing of their bending strength, hardness, porosity, electrical conductivity, and wear behavior, as well as for the microstructural observations and X-ray diffraction analysis (XRD).

![Figure 2. Time–temperature profile of the employed hot-pressing process.](image)

2.3. Tensile and Bending Testing

LF-100 servohydraulic universal testing machine (Walter+bai AG, Löhningen, Switzerland) equipped with an external digital controller (EDC) was used to measure the bending strength. Its values were determined using the DIONPro software (Walter+bai AG, Löhningen, Switzerland) enabling automated recording and statistical analysis of test results. The tensile tests were carried out using a Zwick Z250 apparatus (Zwickroell GmbH, Ulm, Germany), equipped with the contact deformation sensor. The deformation rate was 1 mm/min. Measurement error did not exceed 1%.
2.4. Measurements of Hardness and Relative Density

Hardness (\(H\)) and Young’s modulus (\(E\)) of hot-pressed samples were evaluated by nanoindentation using an MVI Tv/09 Nano Hardness Tester (CSM Instruments, Peseux, Switzerland) at a load of 10 mN and exposure to load for 5 s. The experimental curves recorded for 12–16 indentations were sorted according to indentation depth, enabling assessment of the properties of individual structural components. The indentation curves were processed using the Oliver–Pharr nonlinear curve fit method (ISO 14577–1:2002). The relative density of compact samples was determined by the Archimedes method via hydrostatic weighing using an analytical balance (A&D, Tokyo, Japan). Weight was measured with an accuracy of \(10^{-4}\) g.

2.5. Microstructural and XRD Investigations

The structures of powdered and compact materials were studied by SEM on an S-3400N microscope (Hitachi, Tokyo, Japan) equipped with a NORAN energy-dispersive X-ray spectrometer (Thermo Fisher Scientific, Waltham, MA, USA). The investigation of the fine structure was carried out by TEM JEM 2100 (jeol, Tokyo, Japan). TEM foils were prepared using a PIPS II System for dual ion-beam etching (Gatan, Pleasanton, CA, USA) and by FIB on FEI Quanta 200 3D FIB instrument (FEI, Hillsboro, OR, USA).

X-ray diffraction analysis was performed on a DRON-4 diffractometer (JSC Bourevestnik, St. Petersburg, Russia) using monochromatic CuK\(\alpha\) radiation in a range of angles \(2\theta = 10–120^\circ\).

2.6. Tribological Testing

The tribological tests were carried out using a friction testing machine TRIBOMETER (CSM Instruments, Peseux, Switzerland) according to the “Pin-on-disc” scheme in the following regime: track radius 6.8 mm, load 0.5 N, maximum velocity 10 cm/s, run-length 214 m, and air atmosphere. Three millimeter balls made of Al\(2\)O\(3\) were used as counter-bodies. Three measurements were performed per sample. After the tests, the geometry of wear tracks was investigated using 2D and 3D images, recorded on Wyko NT1100 optic profilometer (Veeco, Plainview, NY, USA). The wear was calculated via Equation (1), implemented in the profilometer software:

\[
WR = \left(\frac{S_{\text{max}}}{n} + \frac{S_{\text{min}}}{n}\right) \times \frac{l}{(F \times S)},
\]

where: 
- \(WR\) — wear, \(\text{mm}^3/(\text{N} \cdot \text{m})\);
- \(S_{\text{max}}\) — section area in a wide segment of the track, \(\text{mm}^2\);
- \(S_{\text{min}}\) — section area in a narrow segment of the track, \(\text{mm}^2\);
- \(n\) — the number of measurements;
- \(l\) — wear track perimeter, \(\text{mm}\);
- \(F\) — load on counterbody, \(\text{N}\); and
- \(S\) — total run, \(\text{m}\).

2.7. Measurements of Electrical Conductivity

Electrical conductivity was measured by the conventional 4-points technique on AKIP-6301/1 installation (JSC “PrisT”, Moscow, Russia) with the measurement precision of \(1 \times 10^{-7}\) Om. Rectangular 40 mm \(\times\) 4 mm \(\times\) 0.1 mm specimens were produced by cutting the hot-pressed specimens with subsequent abrasive thinning. During the machining, specimens were cooled by distilled water to prevent the heating.

3. Results

3.1. Single-Stage and Two-Stage HEBM

The Ti\(\text{H}_2\) powder used in this work was characterized by De Brueckere Mean Diameter \(D\) of 12.04 microns. To investigate the influence of the size of Ti\(\text{H}_2\) particles on the resulting phase composition, structure, and properties, two schemes of HEBM were applied: single-stage HEBM, in which both copper and Ti\(\text{H}_2\) were treated simultaneously for 10 min, and two-state HEBM, in which the Ti\(\text{H}_2\) was first milled for 30 s, then copper was added and the mixture was milled for 10 min. Laser
diffraction measurements demonstrated that pre-milled TiH$_2$ was an order of magnitude finer, with the D of 1.4 microns and 90% of particles being <3 microns (Figure 3).

The two-stage HEBM resulted in the more uniform distribution of TiH$_2$ in the reactive composites (Figure 4). TiH$_2$ particles were immersed into the copper matrix or are located between the copper layers (Figure 4a,c). Single-stage HEBM leads to the more pronounced segregation and agglomeration of TiH$_2$ (Figure 4b,d), probably due to the shielding of large “pockets” filled with TiH$_2$ from the direct impact of steel balls by the layers of ductile copper, especially evident at higher TiH$_2$ content (Figure 4d).

![Figure 3](image-url)  
**Figure 3.** Differential granulometric composition of initial and pre-milled (refined) TiH$_2$.

![Figure 4](image-url)  
**Figure 4.** Reactive composite particles in the Cu-2.5% (a,b) and Cu-10% TiH$_2$ (c,d). TiH$_2$ after two-stage (a,c) and single-stage high energy ball milling (HEBM; b,d).
XRD analysis (not shown) revealed the presence of crystalline TiH₂, copper and cuprite Cu₂O in the ball-milled mixtures, and no traces of titanium or intermetallic compounds. The XRD patterns for Cu-(1–15)% TiH₂ were similar regardless of the applied ball milling protocol or TiH₂ content and differed only in the relative intensity of Cu and TiH₂ peaks.

3.2. Reactive Hot Pressing of Ball-Milled Cu-(0–15)% TiH₂ Mixtures

Compacted specimens were produced by hot pressing of reactive composites at 850 °C in vacuum. Heating up to 700 °C was conducted without the application of pressure to allow for the evaporation of alcohol and desorption of gasses from the surface of powders. All the compacted specimens featured a similar phase composition; the increase in the TiH₂ content in the initial mixture resulted in the more prolific formation of Cu₃Ti₃O (Figure 5). The phase composition of as-milled specimens (not shown) did not depend on the employed milling protocol; after the sintering, specimens produced by single-stage HEBM contained 3–5% of residual Ti (Figure 6).

SEM images of HP specimens (Figure 6) demonstrated that the two-stage HEBM resulted in substantial microstructural refinement and homogenization of the HP alloy. Alloys produced from reactive mixtures Cu-(2.5–15)% TiH₂ after single-stage HEBM contained elongated “islands” of unreacted Ti (black phase on Figure 6c,e,g,i), which were similar in size and shape to the TiH₂ agglomerates in the reactive mixtures (Figure 4d). Layers of Cu₃Ti₃O (0.5–3 µm wide dark-grey phase) separated the Ti islands from the copper matrix (bright phase). Cu₃Ti₃O was also present within the copper matrix but was distributed in a non-uniform fashion (Figure 6g,i). In the alloys fabricated from reactive mixtures after two-stage HEBM, the Ti islands appeared only at TiH₂ content as high as 15% (Figure 6j). At 1–5% TiH₂ content in the initial mixture, Cu₃Ti₃O was uniformly distributed in the copper matrix (Figure 6b,d,f), whereas at 10% TiH₂ (Figure 6h) and 15% TiH₂ (Figure 6j) the aggregation of Cu₃Ti₃O was evident.

Figure 5. XRD patterns for the hot pressing (HP) specimens manufactured with two-stage HEBM of Cu-(0–15)% TiH₂ mixtures.
Figure 6. Microstructures alloys manufactured by HP of reactive mixtures after single stage (a,c,e,g,i) and two-stage (b,d,f,h,j) HEBM of Cu-(1–15)% TiH$_2$ mixture during 10 min.
3.3. Mechanical Properties and Electrical Conductivity of Hot-Pressed Cu-TiH$_2$ Samples

The relative density, three-point flexural strength, and electrical conductivity was measured (Figure 7) and compared with the existing data on spark plasma sintered [9] and hydrogenated Cu-Ti alloys [10–13].

![Figure 7](image_url)

**Figure 7.** Relative density (a), three-point bending strength (b), and conductivity (c) of Cu-Ti alloys produced by HP using single-stage and two-stage HEBM on TiH$_2$ content in the reactive mixture.

The relative density of hot-pressed specimens decreased with increased TiH$_2$ content in the reactive mixture regardless of the employed ball-milling protocol; however, in the case of two-stage milling, this decrease was more pronounced. Surprisingly, despite the evident microstructural heterogeneity (Figure 6), alloys produced using single-stage HEBM demonstrated both higher tensile strength (Figure 7b) and electrical conductivity (Figure 7c). The highest values for strength and electrical conductivity were attained for Cu-10% TiH$_2$ composition processed by single-stage HEBM.

Mechanical properties of individual structural constituents of Cu-10% TiH$_2$ HP samples were measured by nanoindentation (Table 1). Additionally, a copper specimen was produced using the same processing conditions and used as a reference point. The hardness of Cu matrix increased for
4–5 times with the introduction of TiH₂, which might be related to the Zener pinning of the grain boundaries of copper by the in situ formed Cu₃Ti₃O particles.

| Specimen                        | Cu      | Cu₃Ti₃O | α-Ti       |
|---------------------------------|---------|---------|------------|
|                                 | H, GPa  | E, GPa  | H, GPa     | E, GPa | H, GPa  | E, GPa  |
| Cu                              | 1.1 ± 0.1 | 135 ± 10 | -          | -      | -       | -       |
| Cu-10% TiH₂ two-stage HEBM      | 5.5 ± 0.3 | 132 ± 9 | 6.9 ± 0.5  | 165 ± 15 | -       | -       |
| Cu-10% TiH₂ single-stage HEBM   | 5.2 ± 0.4 | 140 ± 12 | 5.8 ± 0.6  | 158 ± 15 | 3.0 ± 0.2 | 110 ± 8 |

Tensile testing of Cu and Cu-10% TiH₂ HP samples revealed 2.5–4.5 higher strength of the Cu-10% TiH₂ specimens compared to the pure copper (Figure 8). The sample produced using single-stage HEBM of Cu-10% TiH₂ mixture was characterized by considerably higher strength—up to 900 MPa, which is comparable to the highly alloyed copper-based materials [29,30] and is slightly higher than the strength of conventional copper–titanium alloys [31,32].

Figure 8. Engineering stress–strain curves for pure copper and HP alloy produced using single-stage and two-stage HEBM Cu-10% TiH₂ composites.

To reveal the origins of higher strength of samples produced by single-stage HEBM of Cu-10% TiH₂, additional TEM investigations were performed.

3.4. TEM Investigation of Hot-Pressed Cu-TiH₂ Samples

Figures 9 and 10 provide the TEM images and EDS mapping of the samples produced using single-stage HEBM (Figure 9) and two-stage HEBM of Cu-10% TiH₂ mixture (Figure 8). TEM investigation of the HP sample produced using single-stage HEBM of Cu-10% TiH₂ revealed a fine-structured copper matrix (grains size 50–150 nm, Figure 9a) interspersed with nanosized Cu₃Ti₃O precipitates (10–20 nm, Figure 9b,c). Both microstructural evaluation (Figure 9b) and EDS mapping (Figure 9c,d) suggest that the Cu₃Ti₃O phase is present in the form of discrete rounded precipitates, which are semi-coherent to the copper matrix (Figure 9e) and relatively uniformly distributed within the copper grains (Figure 9b). The evaluation of TEM images (Figure 9a,c) revealed that the average spacing between Cu₃Ti₃O nanoprecipitates was 30 nm. Therefore, two types of Cu₃Ti₃O inclusions form in the microstructure of alloys produced by single-stage HEBM route: nanosized (1–5 nm) precipitates, which were coherent to the copper matrix (Figure 9) and coarse precipitates, which were located near the incompletely dissolved Ti particles (Figure 6c,e,g,i).
the initial TiH2 content of Cu
fusion of titanium atoms into the copper matrix. Moreover, the overall electrical conductivity of the alloy (Figure 7c).

As a result, the strengthening potential was not fully realized, resulting in lower bending (Figure 7b) and tensile (Figure 8) strength and increased brittleness (Figure 8). Since the Cu3Ti3O phase was considerably less conductive than Cu, the formation of the grain-boundary layers of Cu3Ti3O hampers the electrical conductivity of the alloy (Figure 7c).

Such a difference in the microstructure of the hot-pressed alloys might be related to the higher specific surface of refined TiH2 used in the two-stage HEBM protocol (Figure 3), which provided a higher reactive surface for the diffusion of titanium atoms into the copper matrix. Moreover, the overall content of Cu3Ti3O phase was higher in case of the specimens produced by two-stage HEBM, since all the initial TiH2 was converted into Cu3Ti3O, whereas in case of single-stage HEBM a part of TiH2 upon decomposition forms an independent phase and is not dissolved in the copper matrix (Figure 6c,e,g,i).

3.5. Tribological Performance of Hot-Pressed Cu-TiH2 Alloys

One of the most pivotal characteristics of diamond binders and electrical contacts is the wear resistance. Pin-on-disc tribological testing using the Al2O3 counter-body models the conditions of real-life machining of hard and abrasive materials, such as concrete.
All tested specimens displayed a periodic broadening of the wear track, suggesting a partial pushing of alumina ball into the specimens during the testing. The HP alloy produced using single-stage HEBM of Cu-10% TiH$_2$ mixture demonstrated the best tribological performance among the tested specimens (Figure 11)—its specific wear was nearly an order of magnitude below the value for pure copper and 3.5 times below the value for alloy produced by the two-stage HEBM (Table 2). The coefficient of friction (CoF) for the HP alloy produced using single-stage HEBM of Cu-10% TiH$_2$ was also the lowest among the investigated samples (Table 2).

![Figure 11](image-url)

**Figure 11.** 3D and 2D-images of the wear tracks for the specimens of pure Cu (a), Cu-10% TiH$_2$ mixture produced using single-stage HEBM (b), and HP alloy produced using the two-stage HEBM Cu-10% TiH$_2$ mixture (c).
Investigation of the wear tracks in the HP sample of Cu-10% TiH$_2$ mixture (two-stage HEBM) revealed the formation of fiber-like structures mostly oriented perpendicular to the sliding direction (Figure 12a). The microfibers had a diameter of 100 nm (Figure 12b) and composition close to Cu$_3$Ti$_3$O (Figure 12c). Therefore, two factors could account for the enhanced tribological performance of the sample produced using two-stage HEBM of the Cu-10% TiH$_2$ mixture: increased strength of the alloy (Figure 7) and formation of Cu$_3$Ti$_3$O microfibers, which can ensure a reduction of the coefficient of friction and wear (Table 2) due to a rolling effect and due to the generally lower coefficient of friction in oxide–oxide tribological pairs.

| Sample                  | Normalized Wear, $10^{-5}$ mm$^3$/N/m | Coefficient of Friction (CoF) |
|-------------------------|----------------------------------------|-------------------------------|
| Cu                      | 9.3                                    | 0.86                          |
| Cu-10% TiH$_2$ (single-stage HEBM) | 1.1                                    | 0.6                           |
| Cu-10% TiH$_2$ (two-stage HEBM) | 3.8                                    | 0.74                          |

4. Discussion

Since Cu and TiH$_2$ have drastically different mechanical properties, especially Young’s moduli, the investigated powder mixtures demonstrated different behavior during HEBM. Ductile copper particles were easily deformed, flattened, and welded together upon the collisions with the milling media. The addition of increasing amounts of TiH$_2$ resulted in a gradual shift towards the ductile–brittle mechanical alloying behavior. The brittle particles of TiH$_2$ disintegrate down to a submicron size and get trapped between the layers of copper. Despite the disintegration of initial TiH$_2$ powders during the HEBM, the size of TiH$_2$ particles in the reactive composite particles Cu-TiH$_2$ was distinctly higher in case of single-step HEBM (1–6 µm, Figure 4b,d) as compared to the two-step HEBM (0.1–0.5 µm, Figure 4a,c). This size difference affects the phase and structure formation during the hot pressing of reactive composites.

4.1. Diffusion of Oxygen and Hydrogen in Copper

Interaction between hydrogen and oxygen in copper was previously studied to understand and control the hydrogen embrittlement in alloys with high oxygen contents, such as electrolytic tough pitch (ETP) copper [33]. The hydrogen embrittlement of copper is mainly attributed to the formation of voids as a result of the reduction of copper oxide inclusions or oxygen dissolved in the copper matrix by the diffusing hydrogen. Above the critical point of water (647 K) such reaction forms steam, accelerating the embrittlement process. Embrittlement occurs in two stages: incubation (controlled by

**Figure 12.** SEM image of the wear track in the sample produced using two-stage HEBM of Cu-10% TiH$_2$ mixture (a); TEM image of the individual Cu$_3$Ti$_3$O microfiber (b), and the elemental composition of the Cu$_3$Ti$_3$O microfiber measured by EDS (c).
the oxygen diffusion to internal surfaces) and cracks formation (controlled by hydrogen permeation from the external surfaces to the internal voids).

It was conjectured that the addition of elements with high affinity to hydrogen and oxygen to the copper might influence the hydrogen diffusion in copper by acting as trapping sites and affecting both transient permeation and absorption behavior. A similar trapping effect is expected from the lattice defects in copper, such as vacancies and dislocations [35].

Caskey, et al. [33] noted that oxide impurities in electrolytic tough-pitch copper impeded the hydrogen permeation. After prolonged annealing in hydrogen (24 h at 800 K) and outgassing, the “reduced” electrolytic tough-pitch copper demonstrated the hydrogen permeability similar to oxygen-free copper alloys (1.25 × 10^7 (cm^3/s) (cm/cm^2-atm^1/2)). The authors noted that the annealed specimen was severely blistered due to the formation of pockets of water vapor. The correlation between the amount of absorbed tritium with oxygen content and dependence of permeation transients on both oxygen content and prior treatment was found and associated with reversible and irreversible interactions between hydrogen and dissolved oxygen.

In the case of the sintering of Cu-Cu_2O-TiH_2 reactive composites, the kinetics of reduction of oxygen-based impurities is obviously affected by the length of the diffusion pathway between the source of hydrogen (the decomposing TiH_2 particles) and oxide impurities. To assess the diffusion kinetics of hydrogen and oxygen during the sintering of reactive composites, the data on effective diffusivity of hydrogen and oxygen in copper is provided in Figure 13 based on investigations [33–42] summarized in the recent report of Magnusson and Frisk [43].

![Figure 13](image)

**Figure 13.** Effective diffusion coefficient for copper self-diffusion and diffusion of oxygen and hydrogen in the copper matrix.

Both hydrogen and oxygen diffuse as interstitial elements. The diffusion of hydrogen was previously experimentally studied down to room temperature; oxygen measurements were performed down to 550 °C, and the values are extrapolated to the lower temperatures (Figure 13).

The temperature expressions for hydrogen (D^{FCC}_{H,Cu}) and oxygen (D^{FCC}_{O,Cu}) diffusion in copper are [43]:

\[
D^{FCC}_{H,Cu} = 1.74 \times 10^{-6} \exp\left(-\frac{42,000}{RT}\right) \text{ (m}^2/\text{s) }
\]

\[
D^{FCC}_{O,Cu} = 1.14 \times 10^{-6} \exp\left(-\frac{62,500}{RT}\right) \text{ (m}^2/\text{s) }
\]
The estimations for the employed hot pressing temperature (750 °C) gave the values of $D_{\text{FCC}}^{\text{H},\text{Cu}} = 1.2 \times 10^{-8}$ m$^2$/s and $D_{\text{FCC}}^{\text{O},\text{Cu}} = 7.3 \times 10^{-10}$ m$^2$/s. Since the reactive composites consist of relatively thin copper layers with embedded TiH$_2$ and Cu$_2$O, the two-dimensional Einstein’s relation can be applied to calculate the diffusion length (Equation (4)):

$$D = \frac{s^2}{4t}$$

(4)

where $D$ is the diffusion coefficient (m$^2$/s), $s$ is the diffusion length (m), and $t$ is the time (s).

The calculated diffusion length for hydrogen and oxygen during the isothermal stage of sintering (150 s at 750 °C) is, correspondingly, 2.68 mm and 0.66 mm. Both of these values considerably exceed the characteristic sizes of the reactive composite powders produced by HEBM (50–100 µm, Figure 4), ensuring that during the hot-pressing both diffusing gaseous species can penetrate Cu grains and reach the central regions from evenly distributed tiny precipitates.

One should consider, however, that oxygen has extremely low solubility in copper in the presence of copper oxides [37,43]. The total mass transfer of oxygen will, therefore, be considerably lower than that of hydrogen, even though the mobility of the oxygen is relatively high.

The reduction of copper oxides has been studied in hydrogen gas mixtures corresponding to hydrogen activity close to unity relative 1 atm H$_2$ gas. CuO reduction takes place at 200–300 °C [44], and Cu$_2$O at higher temperatures (350–450 °C) due to its higher stability [45].

Since the hydrogen is a faster diffusor than oxygen, it will diffuse from the decomposing TiH$_2$ particles towards Cu$_2$O inclusions following the concentration gradient. Upon reduction, the as-formed H$_2$O molecule will either leave the composite or become trapped within the copper matrix, serving as the source for the formation of Cu$_3$Ti$_3$O during the cooling stage [21].

4.2. Diffusion of Titanium in Copper

Iijima, et al. [46] studied the interdiffusion coefficients in the Cu-Ti system using the standard Matano analysis of diffusion couples of pure Cu and dilute Cu-Ti alloys. It should be noted that the activation energy $Q = 46.8 \pm 0.5$ cal/mol calculated by Iijima et al. is in good agreement with the previous value $Q = 42–54$ kcal/mol for the volume diffusion of titanium atoms in copper reported in earlier studies of the kinetic behavior using electrical resistivity experiments [47].

The temperature dependence of $D_{\text{FCC}}^{\text{H},\text{Cu}}$ obeys the Arrhenius relation and it is expressed by the following equation [46]:

$$D_{\text{FCC}}^{\text{H},\text{Cu}} = 0.693 + 0.169 \times 10^{-4} \exp\left(-\frac{196 \pm 2 \text{kJ mol}^{-1}}{RT}\right) (\text{m}^2/\text{s})$$

(5)

Using Equations (4) and (5), we estimated the diffusion length for Ti in Cu matrix as 0.067 mm (67 µm), which is comparable with the size of reactive composite powders (Figure 4) and is above the average distance between TiH$_2$ inclusion in the composite powders (5–30 µm), ensuring that the titanium can diffuse into the copper grains during the hot pressing. The smaller size of TiH$_2$ particles in the reactive powders processed by two-step HEBM results in a more active release of H$_2$ during the initial stages of sintering and, correspondingly, a more active reduction of Cu$_2$O and a higher influx of Ti atoms into the copper matrix.

The interdiffusion coefficient in the Cu-rich Cu-Ti solid solution has been shown to depend slightly on the concentration of titanium: the logarithm of the interdiffusion coefficient decreases linearly with the increase of the concentration of titanium. Both the activation energy and the frequency factor for the interdiffusion increase with the increase of the titanium content. A slight shift of the Kirkendall marker toward the Ti-rich side has been found, indicating that titanium atoms diffuse faster than copper atoms in this alloy. However, the formation of Kirkendall voids was not observed [46]. Therefore, the residual
pores observed in hot-pressed specimens in this work are probably the result of the trapping of water vapor formed upon the reduction of Cu$_2$O by H$_2$.

From the onset of Cu$_3$Ti$_3$O formation, a larger concentration of dissolute Ti atoms is available within the copper matrix, leading to the rapid growth of Cu$_3$Ti$_3$O precipitates and formation of relatively thick (up to 0.2 µm) grain boundary layers. The formation of Cu$_3$Ti$_3$O layers afflicts both the mechanical and conductive properties. Since the Cu$_3$Ti$_3$O phase is brittle and substantially less conductive than Cu, the isolation of Cu grains by Cu$_3$Ti$_3$O layers provides a convenient pathway for the propagation of brittle fracture and impedes the electrical conductivity, resulting in both more pronounced brittleness of the alloy (Figure 8) and lesser thermal conductivity (Figure 7c).

Pores play an important role in the mechanical behavior of the materials since they represent the potential sites for the microcracks formation. Pores are commonly evaluated using microstructural studies [48,49]. Open porosity has a pronounced effect on wear characteristics since open pores entrap the wear debris and prevent the formation of large abrasive agglomerates [50]. The porosity of manufactured Cu-TiH$_2$ was in the 2–7% range (relative density 93–98%, Figure 7). At the residual porosity values around 4%, the porosity was usually closed; the inspection of the surface of specimens subjected to tribological testing revealed no open pores (Figure 12a). Therefore, the impact of porosity on the tribological performance of Cu-10% TiH$_2$ alloys appeared to be fairly limited.

The origin of non-linear dependence of both mechanical and conductive properties of Cu-TiH$_2$ samples produced by single-stage HEBM on the TiH$_2$ content (with a maximum at 10%) can be explained by the two competing processes occurring during the decomposition of TiH$_2$: the influx of Ti atoms into the copper matrix and the release of hydrogen, which promotes the consecutive segregation of Ti from the copper matrix during the cooling. Apparently, the optimal amount of hydrogen required to ensure the segregation of 1 mol of Ti atoms from the copper matrix was higher than the amount released during the decomposition of 1 mol of TiH$_2$. Therefore, in a somewhat counter-intuitive fashion, the formation of the $\alpha$-Ti second phase surrounded by Cu$_3$Ti$_3$O layers (Figure 4) was beneficial both for the conductive and mechanical properties of the alloy, since an amount of hydrogen necessary for the separation of Ti from the copper matrix was released during the sintering, whereas the influx of Ti into the copper matrix was limited due to the relatively low reactive surface between the as-formed $\alpha$-Ti and the copper matrix. In that case, further optimization of mechanical and conductive properties of the developed alloys could be achieved by lowering the TiH$_2$ content with the simultaneous introduction of additional H$_2$ sources, such as sintering in H$_2$ atmosphere or hot-pressing of reactive “sandwiches” with two outer layers of TiH$_2$ and a central layer of Cu-TiH$_2$ reactive mixtures (TiH$_2$/Cu-TiH$_2$/TiH$_2$) and subsequent removal of the Ti layers.

4.3. Reproducibility of the Manufacturing Process

Authors want to emphasize that all investigated alloys were manufactured using a specific PMS-1 grade electrolytic copper powder, which was produced by JSC “Uralelectromed” and contained a high amount of Cu$_2$O. Oxide content-wise such powders can be compared to the cheap electrolytic pitch copper, which was widely used in the mid-20th century and was in particular investigated by Caskey, et al. [33]. Application of such copper was complicated by the formation of water vapors due to the hydrogen-induced reduction of cuprous oxides, which resulted in blistering and embrittlement of copper parts (hydrogen embrittlement of copper). In our work, the content of cuprous oxide in the starting powders was controlled by XRD analysis and the deviations were within the measurement errors; however, since cuprous oxide was not introduced into the copper powder in a controllable manner, its fraction may vary. To assess the tolerance of the process, at least three syntheses were performed for each investigated composition using different copper powder batches. No notable deviations between the samples of the similar composition produced from various batches were observed. However, additional investigations are required to assess whether the alloy will demonstrate similar properties if Cu$_2$O is added to an oxide-free copper powder.
4.4. Structural Heterogeneity and the Mechanical Properties of Hot-Pressed Alloys

It should be noted that the achieved level of mechanical properties (ultimate tensile strength of 920 MPa) and conductivity (2.6 × 10⁷ Sm/m) did not surpass the highest previously achieved result—ultimate tensile strength up to 1600 MPa and conductivity up to 5.0 × 10⁷ Sm/m were reported for spark plasma sintered Cu-Ti composites [9]. This discrepancy might have arisen both from over-estimation of the tensile properties in [9] (which were calculated based on Vickers hardness) and from the detrimental effect of coarse Cu₃Ti₃O inclusions and pores in the Cu-Ti alloys manufactured in this work. Although coherent Cu₃Ti₃O precipitates evidently make the Cu matrix strong, the existence of the aforementioned detrimental microstructural features might compromise the structural integrity as the alloy as a physical body. Therefore, further optimization of the employed processing route is required.

5. Conclusions

1. Two high-energy ball-milling (HEBM) protocols were employed for the fabrication of Cu-Ti alloys: single-stage and two-stage ball milling, resulting in an order of magnitude refinement of TiH₂ particles in the reactive mixtures.

2. Single-stage HEBM processing led to the partial retention of Ti in the microstructure of hot-pressed specimens as the α-Ti phase, whereas the two-stage HEBM led to the complete conversion of TiH₂ into the Cu₃Ti₃O phase during the hot pressing.

3. In the HP samples prepared using single-stage HEBM processing, the Cu₃Ti₃O phase formed 10–20 nm precipitates distributed uniformly throughout the copper matrix, whereas two-stage processing led to the formation of 0.1–0.2 μm wide polycrystalline Cu₃Ti₃O layers on the boundaries of Cu grains. As compared to nanosized precipitates, grain-boundary Cu₃Ti₃O layers provided a considerably higher contribution to the resistivity of the alloy, resulting in a lower electrical conductivity (2.6 × 10⁷ Sm/m in case of single-stage HEBM and 0.4 × 10⁷ Sm/m in case of two-stage HEBM).

4. Nanosized Cu₃Ti₃O precipitates provided more effective pinning of the Cu grain boundaries, promoting the formation of finer Cu grains (100–200 nm) in the alloys produced using single-stage HEBM as compared to the alloys produced using two-stage HEBM (1–2 μm Cu grains), which resulted in higher bending strength (up to 950 MPa) and tensile strength (920 MPa).

5. The HP Cu–Ti alloy produced using single-stage HEBM Cu-10% TiH₂ of mixture demonstrated 10 times lower specific wear as compared to copper and 3.5 times lower wear as compared to the alloy produced by the two-stage HEBM (1.1 × 10⁻⁵ and 3.8 × 10⁻⁵ mm³/N/m, correspondingly). This effect was caused by the higher strength of the alloy and formation of Cu₃Ti₃O microfibers in the wear debris, which decreased the friction coefficient against the Al₂O₃ counter-body.

Author Contributions: Study conception and design: S.V., P.A.L.; Acquisition of data: S.V., P.A.L., A.Y.C., A.S.P., M.Y.B., S.I.R., A.S.O., P.V.K.-K.; Analysis and interpretation of data: S.V.; Drafting of manuscript: S.V.; Critical revision: E.A.L., P.A.L. All authors have read and agreed to the published version of the manuscript.

Funding: This was funded by the Russian Science Foundation (Project No. 17-79-20384) in the part of alloy reinforced by Cu₃Ti₃O inclusions manufacturing and characterization, and by the Ministry of Science and Higher Education of the Russian Federation (Project No. 0718-2020-0034 of State assignment) in the part of HRTEM studies.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Datta, A.; Soffa, W.A. The structure and properties of age hardened Cu–Ti alloys. Acta Metall. 1976, 24, 987–1001. [CrossRef]
2. Hameda, A.A.; Blaz, L. Microstructure of hot-deformed Cu–3.45 wt.% Ti alloy. Mater. Sci. Eng. A 1998, 254, 83–89. [CrossRef]
3. Laughlin, D.E.; Cahn, J.W. The crystal structure of the metastable precipitate in copper-based copper–titanium alloys. *Scr. Metall.* 1974, **8**, 75–78. [CrossRef]

4. Soffa, W.A.; Laughlin, D.E. High-strength age hardening copper–titanium alloys: Redivivus. *Prog. Mater. Sci.* 2004, **49**, 347–366. [CrossRef]

5. Semboshi, S.; Sato, S.; Ishikuro, M.; Wagatsuma, K.; Iwase, A.; Takasugi, T. Investigation of precipitation behavior in age-hardenable Cu–Ti alloys by an extraction-based approach. *Metall. Mater. Trans. A* 2014, **45**, 3401–3411. [CrossRef]

6. Semboshi, S.; Nishida, T.; Numakura, H.; Al-Kassaab, T.; Kirchheim, R. Effects of aging temperature on electrical conductivity and hardness of Cu–3 at.% Ti alloy aged in a hydrogen atmosphere. *Metall. Mater. Trans. A* 2011, **42**, 2136–2143. [CrossRef]

7. Suzuki, S.; Hirabayashi, K.; Shibata, H.; Mimura, K.; Ishikuro, M.; Waseda, Y. Electrical and thermal conductivities in quenched and aged high-purity Cu–Ti alloys. *Scr. Mater.* 2003, **48**, 431–435. [CrossRef]

8. Nagarjuna, S.; Balasubramanian, K.;arma, D.S. Effect of Ti additions on the electrical resistivity of copper. *Mater. Sci. Eng. A* 1997, **225**, 118–124. [CrossRef]

9. Eze, A.A.; Jamiru, T.; Sadiku, E.R.; Durowoju, M.O.; Kupolati, W.K.; Ibrahim, I.D.; Obadele, B.A.; Olubambi, P.A.; Diouf, S. Effect of titanium addition on the microstructure, electrical conductivity and mechanical properties of copper by using SPS for the preparation of Cu-Ti alloys. *J. Alloys Compd.* 2018, **736**, 163–171. [CrossRef]

10. Semboshi, S.; Numakura, H.; Gao, W.L.; Suda, H.; Sugawara, A. Aging of Copper-Titanium Dilute Alloys in a Hydrogen Atmosphere. *Mater. Sci. Forum* 2003, **45**, 341–345. [CrossRef]

11. Semboshi, S.; Takasugi, T. Fabrication of high-strength and high-conductivity Cu–Ti alloy wire by aging in a hydrogen atmosphere. *J. Alloys Compd.* 2013, **580** (Suppl. 1), S397–S400. [CrossRef]

12. Olubambi, P.A.; Diouf, S. Effect of Prior Cold-Working on Strength and Electrical Conductivity of Cu-Ti Dilute Alloy Aged in a Hydrogen Atmosphere. *Mater. Sci. Forum* 2010, **654–656**, 1315–1318. [CrossRef]

13. Semboshi, S.; Nishida, T.; Numakura, H. Microstructure and mechanical properties of Cu–3 at.% Ti alloy aged in a hydrogen atmosphere. *Mater. Sci. Eng. A* 2009, **517**, 105–113. [CrossRef]

14. Olson, G.B. Computational Design of Hierarchically Structured Materials. *Science* 1997, **277**, 1237–1242. [CrossRef]

15. Ming, K.; Bi, X.; Wang, J. Strength and ductility of CrFeCoNiMo alloy with hierarchical microstructures. *Int. J. Plast.* 2019, **118**, 255–268. [CrossRef]

16. Thompson, B.R.; Horozov, T.S.; Stoyanov, S.D.; Paunov, V.N. Hierarchically structured composites and porous materials from soft templates: Fabrication and applications. *J. Mater. Chem. A* 2019, **7**, 8030–8049. [CrossRef]

17. Song, G.; Hong, S.J.; Lee, J.K.; Song, S.H.; Hong, S.H.; Kim, K.B.; Liaw, P.K. Optimization of B2/L21 hierarchical precipitate structure to improve creep resistance of a ferritic Fe-Ni-Al-Cr-Ti superalloy via thermal treatments. *Scr. Mater.* 2019, **161**, 18–22. [CrossRef]

18. Hasan, M.N.; Liu, Y.F.; An, X.H.; Gu, J.; Song, M.; Cao, Y.; Li, Y.S.; Zhu, Y.T.; Liao, X.Z. Simultaneously enhancing strength and ductility of a high-entropy alloy via gradient hierarchical microstructures. *Int. J. Plast.* 2019, **123**, 178–195. [CrossRef]

19. Olson, G.B. Systems design of hierarchically structured materials: Advanced steels. *J. Comput.-Aided Mater. Des.* 1998, **4**, 143. [CrossRef]

20. Potanin, A.Y.; Vorotilo, S.; Pogozhev, Y.S.; Rupasov, S.I.; Lobova, T.A.; Levashov, E.A. Influence of mechanical activation of reactive mixtures on the microstructure and properties of SHS-ceramics MoSi2–HfB2–MoB. *Ceram. Int.* 2019, **45**, 20354–20361. [CrossRef]

21. Vorotilo, S.; Potanin, A.Y.; Pogozhev, Y.S.; Levashov, E.A.; Kochetov, N.A.; Kovalev, D.Y. Self-propagating high-temperature synthesis of advanced ceramics MoSi2–HfB2–MoB. *Ceram. Int.* 2019, **45**, 96–107. [CrossRef]

22. Potanin, A.Y.; Vorotilo, S.; Pogozhev, Y.S.; Rupasov, S.I.; Loginov, P.A.; Shvyndina, N.V.; Sviridova, T.A.; Levashov, E.A. High-temperature oxidation and plasma torch testing of MoSi2–HfB2–MoB ceramics with single-level and two-level structure. *Corros. Sci.* 2019, **158**, 108074. [CrossRef]

23. Vorotilo, S.; Levashov, E.A.; Kurbatkina, V.V.; Kovalev, D.Y.; Kochetov, N.A. Self-propagating high-temperature synthesis of nanocomposite ceramics TaSi2–SiC with hierarchical structure and superior properties. *J. Eur. Ceram. Soc.* 2018, **38**, 433–443. [CrossRef]
24. Vorotilo, S.; Logiachev, P.A.; Kovalev, D.Y.; Levashov, E.A. DFT-Driven design of hierarchically structured, strong and highly conductive alloys in Cu–Ti system via in situ hydration-re-oxidation. *J. Alloys Compd.* 2020, 832, 154823. [CrossRef]

25. Sawa, K. Sliding Electrical Contacts and Materials. In *Encyclopedia of Tribology*, Wang, Q.J., Chung, Y.W., Eds.; Springer: Boston, MA, USA, 2013.

26. Bateni, M.R.; Ashrafizadeh, F.; Szpunar, J.A.; Drew, R.A.L. Improving the tribological behavior of copper through novel Ti–Cu intermetallic coatings. *Wear* 2002, 253, 626–639. [CrossRef]

27. Sakamoto, Y.; Takao, K. The electrochemical determination of diffusion coefficients. *J. Phys. Chem. Solids* 1981, 42, 795–798. [CrossRef]

28. Caskey, G.R.; Dexter, A.H.; Holzworth, M.L.; Louthan, M.R.; Derrick, R.G. The effect of Oxygen on Hydrogen Transport in Copper. *Corrosion* 1976, 32, 370–374. [CrossRef]

29. Ishikawa, T.; McLellan, R.B. The diffusivity of hydrogen in copper at low temperatures. *J. Phys. Chem. Solids* 1985, 46, 445–447. [CrossRef]

30. Perkins, W.G.; Begeal, D.R. Permeation and diffusion coefficients in pure copper at near room temperature by means of tritium tracer techniques. *Trans. Metall. Soc. AIME* 1958, 211, 211–217. [CrossRef]

31. Maghnusson, H.; Frisk, K. Thermodynamic evaluation of Cu-H-O-S-P system. *Berichte der Bunsengesellschaft für Physikalische Chemie* 1972, 76, 863.

32. Albert, E.; Kirchheim, R. Diffusivity of oxygen in copper. *Scr. Metall.* 1981, 15, 673–677. [CrossRef]

33. Caskey, G.R.; Dexter, A.H.; Holzworth, M.L.; Louthan, M.R.; Derrick, R.G. The effect of Oxygen on Hydrogen Transport in Copper. *Corrosion* 1976, 32, 370–374. [CrossRef]

34. Ishikawa, T.; McLellan, R.B. The diffusivity of hydrogen in copper at low temperatures. *J. Phys. Chem. Solids* 1985, 46, 445–447. [CrossRef]

35. Sakamoto, Y.; Takao, K. The electrochemical determination of diffusion coefficient and solubility of hydrogen in copper. *J. Phys. Chem. Solids* 1981, 42, 285–290. [CrossRef]

36. Perkins, W.G.; Begeal, D.R. Permeation and diffusion in hydrogen in ceramvar, copper and ceramvar-copper laminates. *Berichte der Bunsengesellschaft für Physikalische Chemie* 1972, 76, 863.

37. Magnusson, H.; Frisk, K. Thermodynamic evaluation of Cu-H-O-S-P system. In *Phase Stabilities and Solubilities for OHP-Copper*; SKB TR-13-11; Svensk Kärnbränslehantering AB: Stockholm, Sweden, 2013.

38. Albert, E.; Kirchheim, R. Diffusivity of oxygen in copper. *Scr. Metall.* 1981, 15, 673–677. [CrossRef]

39. Caskey, G.R.; Dexter, A.H.; Holzworth, M.L.; Louthan, M.R.; Derrick, R.G. The effect of Oxygen on Hydrogen Transport in Copper. *Corrosion* 1976, 32, 370–374. [CrossRef]

40. Ramana Rao, A.V.; Tare, V.B. Diffusion coefficient of oxygen in solid copper by the steady state current method using a solid electrolyte. *Zeitschrift für Metallkunde* 1973, 63, 70–73.

41. Országh, J.; Bouillon, F. Diffusion de l’oxygène dans le cuivre monocristallin. *Mémoires Scientifiques de la Revue de Métallurgie* 1973, 70, 319–325. (In French)

42. Horinouchi, H.; Shinohara, H.; Otsuka, T.; Hashizume, K.; Tanabe, T. Determination of hydrogen diffusion and permeation coefficients in pure copper at near room temperature by means of tritium tracer techniques. *J. Alloys Compd.* 2013, 580, S73–S75. [CrossRef]

43. Magnusson, H.; Frisk, K. Self-Diffusion and Impurity Diffusion of Hydrogen, Oxygen, Sulphur and Phosphorus in Copper. Technical Report TR-13-24; Svensk Kärnbränslehantering AB: Stockholm, Sweden, 2013.

44. Jelić, D.; Tomić-Tucaković, B.; Mentus, S. A kinetic study of copper(II) oxide powder reduction with hydrogen, based on thermogravimetry. *Thermochim. Acta* 2011, 521, 211–217. [CrossRef]

45. Tillander, U.; Ragnhild, A.E.; Seetharaman, S. Kinetics studies of hydrogen reduction of Cu2O. *Zeitschrift für Metallkunde* 2006, 97, 72–78.

46. Iijima, Y.; Hoshino, K.; Hirano, K. Diffusion of titanium in copper. *Metall. Trans. A* 1977, 8, 997–1001. [CrossRef]

47. Korotayev, A.D.; Tsinenko, O.V.; Protasov, A.T. Kinetics of continuous and discontinuous decomposition in a copper-titanium alloy. Pt. 1. *Fiz Met. Metalloved.* 1968, 26, 789.

48. Kosyanov, D.Y.; Yavetskiy, R.P.; Parkhomchenko, S.V.; Doroshenko, A.G.; Vorona, I.O.; Zavjalov, A.P.; Zak Arena, A.M.; Vornovskikh, A.A. A new method for calculating the residual porosity of transparent materials. *J. Alloys Compd.* 2019, 781, 892–897. [CrossRef]
49. Bidulská, J.; Bidulský, R.; Actis Grande, M.; Kvačkaj, T. Different Formation Routes of Pore Structure in Aluminum Powder Metallurgy Alloy. *Materials* **2019**, *12*, 3724. [CrossRef] [PubMed]

50. Bidulský, R.; Grande, M.A.; Bidulská, J.; Vlado, M.; Kvačkaj, T. Wear Mechanism of Chromium Pre-Alloyed Sintered Steel. *High Temp. Mater. Process.* **2009**, *28*, 175–180. [CrossRef]

© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).