BMSM

Bulletin of Materials Science & Metallurgy

Periodical Scientific Journal of UCTEA Chamber of Metallurgical and Materials Engineers

Volume 1, Issue 3, 2024, Pages 25-30 Received: 15 November 2024 Accepted: 25 December 2024

https://doi.org/10.70342/QYXE2962

Research Article

Effect of Aluminum Content on the Properties of Spark Plasma Sintered Tungsten, Niobium, Vanadium, Molybdenum & Aluminum Refractory High Entropy Alloys

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Abstract

Four samples with 6 hours MA durations were prepared with the Al concentrations of 0.25, 0.5, 0.75 and 1 for spark plasma sintering. XRD analysis for both pre-sintered and sintered samples showed single BCC phase. Equiaxed grain morphology and homogenous distribution of the elements were detected by SEM/EDS investigations. Highest hardness value was acquired as 1.5 GPa from Al 0.5 M sample.

Keywords

High Entropy Alloys, Refractory, Composites, Metals, Multi-metallic Cocktails

1. Introduction

High entropy alloys (HEAs) have created an important paradigm shift and change in alloy design processes. In recent years, new HEAs based on refractory elements have been geared towards high temperature applications. Refractory high entropy alloys (RHEAs) are materials that have superior high temperature properties (above 800ºC) such as strength and hardness [1-2], resistance to oxidation, wear and corrosion [3-5]. Even some RHEAs can maintain strength values up to 1600ºC [6-7]. These exceptional features are in high demand in the aviation and aerospace industries as load-bearing or thermal protection structures.

Conventional synthesis methods of RHEAs are primarily focused on vacuum arc-melting, which produces dendritic microstructures and coarse grain size, resulting in undesirable final properties. In recent years, mechanical alloying (MA) has emerged as a superior technique over vacuum arc melting for the synthesis of refractory high entropy alloys due to several key advantages. Firstly, mechanical alloying allows for the production of RHEAs with a greater variety of compositions and alloying elements [8]. Secondly, mechanical alloying offers excellent homogeneity at the atomic level, resulting in a more uniform distribution of alloying elements in the microstructure of RHEAs which enhances the overall mechanical properties, such as hardness and tensile strength of the final alloy [9-10]. Furthermore, mechanical alloying promotes the formation of metastable phases and solid solutions, which are desirable for the development of novel RHEAs with enhanced properties. The high-energy milling involved in mechanical alloying induces severe plastic deformation and facilitates the synthesis of new phases, leading to improved mechanical and thermal stability. [11-12].

The combined utilization of mechanical alloying and spark plasma sintering (SPS) has shown great potential in the development of RHEAs with exceptional properties. Recent studies have focused on exploring the synergistic effects of these techniques to tailor the microstructure and enhance the mechanical and thermal properties of refractory alloys. Mechanical alloying, through high-energy ball milling, promotes the formation of nanocrystalline structures and the homogeneous distribution of multiple principal elements in near-equimolar ratios. Subsequently, spark plasma sintering facilitates the rapid consolidation of mechanically alloyed powders, resulting in fully dense alloys with refined microstructures and improved mechanical properties. The combined approach has demonstrated promising results in the development of RHEAs based on tungsten (W) combined with elements such as molybdenum (Mo), niobium (Nb), vanadium (V), and aluminum (Al). These alloys exhibit enhanced strength, excellent thermal stability, and improved resistance to wear and corrosion. The MA-SPS combination has proven successful in achieving controlled phase formation, homogeneous mixing, and the preservation of nanoscale features, enabling the production of high-performance refractory alloys for applications in extreme temperature environments [1-2-3].

In this present work, concept of RHEA was tested by spark plasma sintering W, Nb, V, Mo refractory elements and generating HEA with an addition of Al element to achieve better mechanical properties and homogeneous distribution of the elements. Four samples were produced and seperated among each other for their Al concentrations. The produced samples are as follows; 6 hours MA'd $WNbMoVAl_x$ where x is, 0.25, 0.5, 0.75 and 1. MA duration of 6 hours was selected as the optimum time since from the literature it was obtained that 2 hours of mechanical alloying causes elemental powders to finally dissolve into crystal structures with single phases, 4 hours and 6 hours are the critical durations for mechanical alloying since single-phase crystal structures complete their formation. However, beyond 6 h mechanical alloying, it was observed that fine particles obtained by mechanical alloying may start to agglomerate and form coarser particles [10].

2. Experimental Procedure

The starting materials used in this investigation were high purity (> 99.6 %) W (supplied from AEM™, particle size < 45 microns), Mo, Nb and V (supplied from Jinzhou Haixin Metal Materials™ Co. Ltd., particle size < 10 microns) and Al powders. Two groups of powder samples were blended, each blend weighing 12 g. The experimental group is constituted of equimolar amounts of the refractory elements, whereas the amount of Al is increased systematically from zero to equimolar and is referred to as $WNbMoVAl_x$ (x = 0, 0.25, 0.50, 0.75 and 1.0). Powder batches were mixed in a WAB™ T2C Turbula mixer for about 1 h. WC vials and WC balls were cleaned with isopropyl ethanol and the pre-cleaned WC vials and milling balls were coated with equimolar WNbMoV powders via mechanical alloying for 4 hours before each process to further reduce the chances of contamination. After that, the prepared powder mixtures were placed in pre-cleaned WC vials (50 ml) with WC balls and the filled vials were closed and sealed under high purity Ar (Linde™, 99.999%) atmosphere in a MBraun™ glove box. Care was taken to ensure that the O_2 and humidity inside the glove box did not exceed 50 ppm and 1 ppm, respectively. Mechanical alloying experiments were carried out with a ball-to-powder (BPR) weight ratio of 10:1 with the duration of 6 h in a Spex™ 8000D dual mill rotated at 1200 rpm. Mechanically alloyed samples were spark plasma sintered at 1500^0C under 35 MPa pressure for 10 minutes in a FCT™ GmbH brand HPD-50 model SPS furnace. The density values of both the MA'd and SPS'd samples were tested by Archimedes' principle. Vickers hardness tests of both MA'd and SPS'd samples were carried out in a Shimadzu™ HMV microhardness tester. A total of 25 indentations were taken from the samples at 8 different corner and edge locations using a load of 9 N for 15 seconds.

In order to determine the phase characteristics of the $WNbMoVAl_x$ (x = 0, 0.25, 0.50, 0.75 and 1.0) refractory high entropy alloys, CALPHAD FactSage^{TM} 7.2 simulation program was used. The correlation of the simulation data and the experimental data was tested via XRD for both mechanically alloyed and spark plasma sintered samples. From the simulation, it is deduced that the addition of Al atoms increases the BCC2 phase and elevates the BCC transformation temperature of this phase to 1000^0C. As the incremental addition of Al atoms increases, the formation of intermetallic compounds of $AlMo_3$, Al_3Nb, and Al_8Mo_3 are predicted to emerge. X-ray diffractometry (XRD) and scanning electron microscopy (SEM) investigations were carried out to characterize the MA'd and SPS'd refractory high entropy alloy samples. A Bruker™ D8 Advanced Series X-ray diffractometer was operated to identify the crystalline phases using CuKα (λ = 1.5406 Å) radiation (0.154 nm, 35 kV, 40 mA) with a scanning speed of 2/min. Microstructural characterizations and spectral chemical analyses of the MA'd and SPS'd RHEAs were carried out using a Thermo Scientific Quattro scanning electron microscope (15 kV) coupled with an energy-dispersive X-ray spectrometer (EDX).

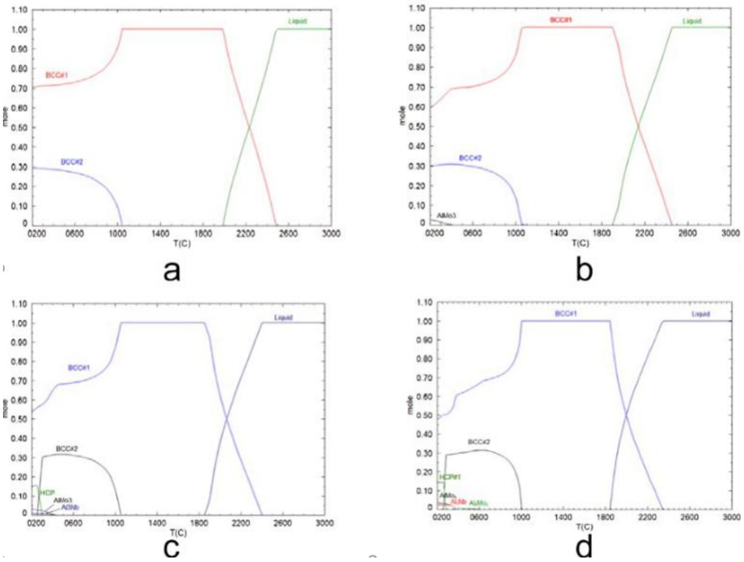


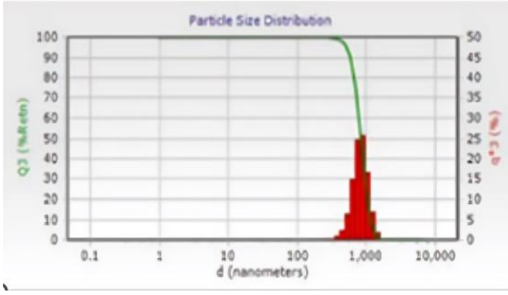
Figure 1. Phase formation diagrams by CALPHAD model for a)$Al_{0.25}WNbMoV$, b)$Al_{0.5}WNbMoV$,c)$Al_{0.75}WNbMoV$, d)AlWNbMoV compositions.

Particle sizes were measured in deionized water media using a Malvern™ Laser particle size analyzer (PSA). Before the PSA analysis, powders in distilled water were dispersed using a Bandelin Sonopuls™ ultrasonic homogenizer.

3. Results and Discussion

3.1. Characterization of the powders

Figures 2a and 2b show the particle size distributions of the equimolar WVMoNbAl RHEA powders MA'd for 2 h and 6 h, respectively. It can be deduced that as the MA duration increases, the particle sizes of the MA'd RHEA powders decrease. Further, the 6 h MA'd sample displays a Gaussian-like average particle size distribution.



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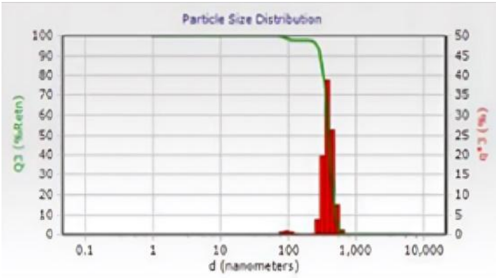

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Figure 2. Particle size distributions of the equimolar WVMoNbAl refractory high entropy alloy: a) MA'd for 2 h and b) MA'd for 6 h.

In the light of the particle size distributions 6 h was selected as the optimum MA duration for further investigations prior to consolidation.

XRD patterns of $WVMoNbAl_x$ refractory high entropy alloy were investigated for their different compositions. Figure 3, shows the XRD patterns for, 0.5, and 1 Al mole fractions having $WVMoNbAl_x$ refractory high entropy alloys for MA durations of 6 hours. It is important to note that these patterns belong to the samples which are mechanically alloyed and spark plasma sintered. Single BCC dominant phase was observed with some minor carbide phases which is most likely the result of MA and/or SPS processes.

Density and hardness measurements were conducted on the spark plasma sintered $WVMoNbAl_x$ RHEA samples. For different Al concentrations the theoretical density, experimented density and relative density values were given in **Error! Reference source not found.**. The experimental density values were gauged with Archimedes' method by weighting the samples in air and water settings. It can be deduced that the porosity amount of $WVMoNbAl_x$ RHEAs produced by mechanical alloying and spark plasma sintering methods within the scope of the experiment is less than 15%. Porosity values may depend on many factors, such as external gases that have not been sufficiently cleaned in the vacuum chamber before mechanical alloying, insufficient mechanical alloying.

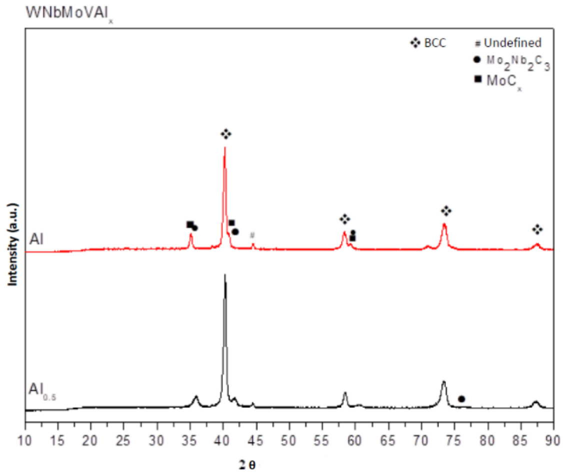


Figure 3. XRD patterns of SPS'd $WVMoNbAl_x$ refractory high entropy alloy with 6 hours of mechanical alloying and 0.5, 1 molar Al concentrations.

Considering these conditions, it is not possible to reach a definite conclusion about the measured densities and mechanical alloying times of the tested compositions. However, with the increase of aluminum concentration, the overall density of the sample decreases as expected, since the density values of the MA'd and spark plasma sintered, WVMoNb powders showed higher Archimedes density values which are; 10.11, 10.45, 10.81, 10.24, 10.34 g/cm^3 respectively.

3.2. Mechanical properties

Vickers hardness values of mechanically alloyed and spark plasma sintered, at 1500^0C, under 35 MPa for 10 minutes, samples were tested and compared according to their Al concentrations. **Error! Reference source not found.**1, shows the Vickers hardness values, along with the relative densities of each alloy tested through this research.

From the data given it can be deduced that the increasing addition of Al element increases the hardness value of the samples. This depiction is based on the comparison of these samples among each other and with the WNbMoV alloys from the literature [5]. Solid solution hardening along with the severe lattice distortion caused by the Al atoms, as well as the BCC stabilizer effect causes hardening on the alloys and finer grain sizes with the increased MA durations are the mechanisms behind the hardness results [10-11-12]. The Vickers hardness values of $WVMoNbAl_x$ RHEAs samples at various aluminum concentrations were obtained by hardness tests under a 9 N load for 15 seconds and performed at an average of 25 different points for each sample. In the light of the results obtained, it was concluded that the solid solution hardening mechanism was effective as a result of the addition of aluminum to the sample [11-12].

Table 1. Vickers hardness and relative density values of SPS'd $WVMoNbAl_x$ RHEA for different Al concentrations. (a: non-SPS'ed)

Alloy	MA Duration	Relative % Density	Hardness (GPa)	Standard Deviation
$WVMoNbAl_{0.25}$	6 hours	89.40	13.6	0.72
$WVMoNbAl_{0.5}$	6 hours	90.39	15.0	0.676
$WVMoNbAl_{0.75}$	6 hours	98.66	14.11	0.61
WVMoNbAl	6 hours	90.30	12.31	0.86
WVMoNbAl	0 hours	89.15	7.65	0.94
WVMoNbAl[a]	6 hours	60.31	-	-
WVMoNbAl[a]	8 hours	62.66	-	-

These results became especially predominant when compared with the WVMoNb base alloy, since the base alloy with 6 hours MA duration had hardness value of 11.74 GPa, which was previously determined within the scope of TÜBİTAK 119M980 project, conducted by ITU PML.

Aluminum atoms cause distortions in the lattice structure after finding a place for themselves among the crystal structure formed by the base alloy elements in the quaternary system [11-12-13]. Dislocation movements are restricted due to the escalation of lattice potential resulting in an increment in material hardness and strength [11-12-13]. When the hardness values of the samples were compared, it was observed that the highest hardness value was obtained for the RHEA containing 0.5 Al. It was clear that the effect of SPS on the hardness values of the samples was undeniable.

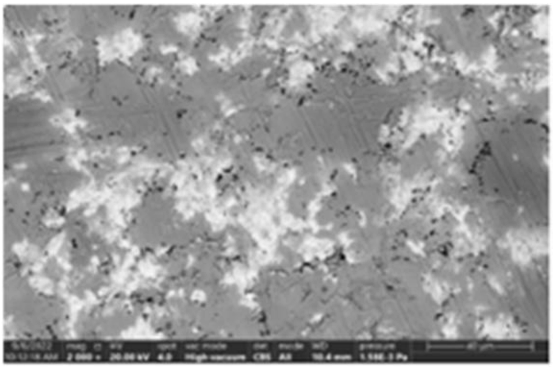
Wear tests were carried out with the parameters of 4 N load, 2 mm length, 6 mm/s sliding speed for 50 meters. 6 mm Al_2O_3 balls were used as a counterface. Data for friction coefficients, wear track areas, and wear rate were gathered and represented in Table 2. When the data from the table is examined, 6 hours and 8 hours of mechanically blended samples yield very close values, and comparison between 0.5 Al and 1 Al can be observed. Mechanical alloying duration along with Al content has a positive effect on wear properties of the RHEA.

Table 2. Volume losses and wear rates of $WMoNbVAl_x$ RHEA samples.

Alloy	MA Duration	Wear Track Area (mean, nm^2)	Wear Rate (mm^2/N)
WVMoNbAl	2 hours	74.3	$0,74x10^{-15}$
WVMoNbAl	6 hours	34.8	$0,348x10^{-15}$
WVMoNbAl	8 hours	32.7	$0,32x10^{-15}$
$WVMoNbAl_{0.5}$	6 hours	85.67	$0,85x10^{-15}$

3.3.Microstructure

SEM/EDS analyses of the samples show the distribution of the elements throughout the alloy. From the Fig4, the as-blended samples grain morphology can be observed. The dark and light grey phases seen in the 2000x magnification image are the phases where the main matrix and the tungsten rich areas are dense respectively. The dark grey areas are the BCC matrix phases and the light grey areas are WC-rich areas. When the overall composition of the sample was taken into consideration, the amount of light grey areas is very low that it can be neglected.



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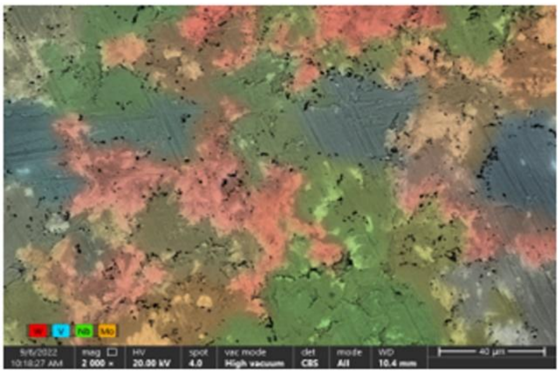

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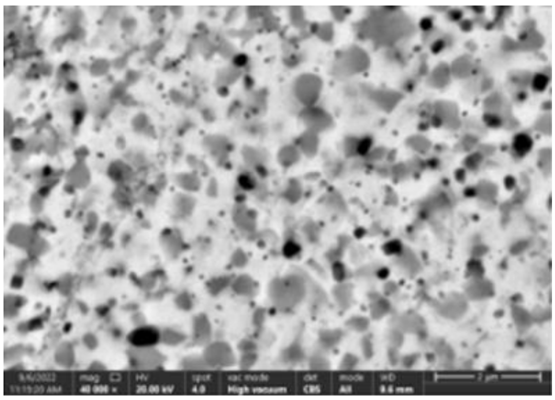
Figure 4. As-blended, spark plasma sintered, equimolar WVMoNbAl RHEAs 2000x EDS/SEM mappings.

When the EDS analyzes are examined from the Figure5, it can be said for the 0.25 M, 6 h MA'd sample, it has a largely homogeneous element distribution as it is shown in **Error! Reference source not found.**3. It can be deduced that with MA duration, the alloy becomes more homogenously distributed and grain size is reduced.



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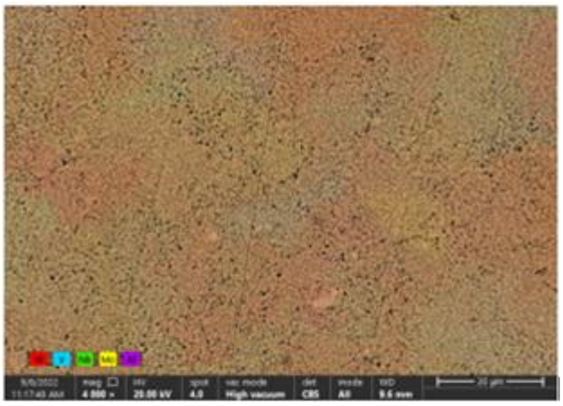

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Figure 5. Images of 0.25M WVMoNbAl$_x$ RHEA with 6 hours MA duration a)40000x b)4000x EDS/SEM.

Table 3. Elemental distribution of the WVMoNbAl$_x$ RHEA with 0.25 Al concentration and 6 hours MA duration.

Alloy	Atomic %	Atomic % Error	Weight %	Weight % Error
Al	5.9	0.2	1.6	0.0
V	23.3	0.1	11.6	0.0
Nb	26.1	0.6	23.8	0.6
Mo	20.6	0.0	19.4	0.0
W	24.2	0.2	43.6	0.3

4. Conclusion

In this work, a total of 8 WVMoNbAl$_x$ refractory high entropy alloys were produced using mechanical alloying and spark plasma sintering techniques at different Al concentrations (0.25, 0.5, 0.75, and 1.0 wt.%), followed by their characterization investigations and mechanical tests. The effects of the Al element on the properties of the produced RHEA were investigated.

On the basis of the results reported in work, the following conclusions can be drawn:

From the data retrieved from the literature, 6 hours of mechanical alloying duration was found to be the optimum duration for the alloying process. Hardness tests were carried out under a 9 N load for 15 seconds and 25 tests from different points were operated for each sample. These results have indicated the increases in hardness values of the WVMoNbAl$_x$ can be attributed to increased MA duration and Al concentration (to a certain extent). The highest hardness values of 15 GPa and 14.11 GPa belong to the WVMoNbAl$_x$ (x=0.5, 0.75) RHEA samples mechanically alloyed for 6 hours, respectively. From the results it can be inferred that Al atoms trigger the solid solution hardening mechanism in the alloy by merging into the lattices, causing distortions and preventing dislocation movements leading to increased hardness of the alloys. Wear test data shows that, 6 hours and 8 hours of mechanically blended samples yield very close values, and comparison between 0.5 Al and 1 Al can be observed. Mechanical alloying duration along with Al content has a positive effect on wear properties of the RHEA.

Microstructures and elemental distribution of the samples were investigated. Almost every sample had a homogenous distribution of the elements throughout the alloy. The as-blended sample had the least homogenous distribution of the elements compared to the other samples, proving the effect of MA on elemental distribution. Overall, the observed phase was the single BCC phase for spark plasma sintered samples. The scanning electron microscope images showed three distinct regions on them, color-coded as; light grey, dark grey, and black regions. Those regions were composed of tungsten-rich, BCC matrix, and porosities. Therefore, SEM images of the samples are coherent with the XRD patterns of the samples.

Authors' Contributions

Project administration: Duygu Ağaoğulları, M. Lütfi Öveçoğlu; Supervision: Duygu Ağaoğulları, M. Lütfi Öveçoğlu; Writing-original draft preparation: Erman Yaman, M. Lütfi Öveçoğlu; Writing-review and editing: M. Lütfi Öveçoğlu; Conceptualization: Duygu Ağaoğulları, M. Lütfi Öveçoğlu; Investigation: Erman Yaman

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This study is a part of a research project entitled "Synthesis of refractory high entropy WNbMoVCr$_x$Al$_y$ (x, y = 0 - 1,0) alloys via mechanical alloying, their densification and sintering using various processes and related characterization investigations" funded by the Technological and Research Council of Turkey (TÜBİTAK) with a project number of 119M980 and this is greatly appreciated. We would like to thank Prof. Dr. Hüseyin Çimenoğlu for allowing us to access his laboratory facilities and Mertcan Kaba in carrying out the wear tests. Additionally, we want to thank Assoc. Prof. Dr. Erhan Ayas and Kübra Gürcan Bayrak at Eskişehir Technical University for performing the spark plasma sintering experiments and Assoc. Prof. Dr. Bedri Baksan at Osmangazi University for the high temperature compression tests of the present study.

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