60.0 FUNDAMENTALS OF RECRYSTALLIZATION IN BINARY Nb-ALLOYS

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60.1 Project Overview and Industrial Relevance

Niobium is a relatively lightweight refractory metal with a wide variety of applications, including the manufacturing of refractory alloys, refractory multi-principal element alloys (RMPEA), and superconducting components. Niobium based superconductors such as Nb_3Sn or NbTi are type II superconductors favored in industry for their high magnetic flux densities, commercial reliability, and availability[60.1-60.2]. In particular, Nb_3Sn has proven itself to be a powerful superconductor, with new strides in alloy development pushing its capabilities even further. Recent studies have shown additions of Hafnium to Nb alloys used in making Nb_3Sn wires improved performance while in the superconducting state [60.1-60.2]. These Hf additions to Nb result in the suppression of grain growth and recrystallization behavior by raising the effective recrystallization (Rx) temperature, resulting in the stabilization of grain growth kinetics during annealing and Nb_3Sn formation temperatures. This leads to the stabilization of heavily worked structures at the Nb_3Sn formation temperatures, allowing for an increase in grain boundary diffusion paths for Sn into the base Nb alloy [60.3]. As such, the final microstructure in the superconducting phase will have a finer grain structure, causing an increase in flux pinning and ultimately improving its performance as a superconductor.

Given these recent findings and the reputed capabilities of Nb_3Sn superconductors, it has become the superconductor of choice for the development of future particle accelerators [60.2] as well as a variety of other industrial applications in high energy physics and medicine. As such, manufacturers will need to be capable of meeting the increase in demand in an economically feasible way. Unfortunately, Hf is a constrained resource and could become a major limiting factor for manufacturers in the future. Therefore, cost effective alternative alloying elements capable of producing similar results without detrimental formability effects will need to be identified. To do this, a series of binary Nb alloys will be created with elements including Ti, Zr, Hf, V, Ta, Mo, W, and Re. These alloys will be subjected to varying degrees of deformation (>60%), with hardness measurements being taken to observe work hardening behavior, before being subjected to various heat treatments in the Gleeble® thermal-mechanical simulator. Scanning electron microscopy (SEM) and electron backscattered diffraction (EBSD) will be used to observe the resulting microstructural evolution and will allow for a fundamental understanding of how these alloying elements affect the recrystallization parameters of Nb. In doing so, this project aims to provide useful information for future developments of Nb-based superconductors and RMPEA applications.

60.2 Previous Work

Work began with a literature review spanning the topics of superconductivity, phase stabilities, and recrystallization and mechanical behavior of refractory alloys. Doing so has helped to provide a state-of-the-art understanding of the key issues and variables relevant to this study, as well as current research capabilities, terminology, and techniques. Furthermore it has given a basis for selecting alloying elements and compositions of interest to test. Various experiments over the years outline solid solution strengthening elements, such as rhenium or zirconium [60.4-60.5], as responsible for an inhibition of grain growth and recrystallization behavior in Nb alloys. In addition to solid solution strengthening affecting recrystallization parameters, elements known for relatively high thermodynamic activity such as V, Ti, or Hf will form nonmetallic compounds with impurities in the Nb, which can cause similar effects [60.4]. As such there is reason to believe that several of the elements selected for testing may be effective as a replacement for Hf. The literature review process is ongoing.

In addition to sourcing information from literature, binary phase diagrams were generated in ThermoCalc™ to observe phase stabilities and solubility for a total of 18 different alloying elements. Many of these elements in question did not pass this initial litmus test as they either formed secondary phases or brittle intermetallic compounds. Elements that formed solid solutions with Nb at low concentrations were chosen to be used for the initial round of binary tests, with compositions likely to range between 2 - 5 wt.% per alloying element. These compositions were chosen based on values from various commercial Nb based alloys, which attempt to maintain a comparable ductility to pure Nb, as well as keep alloying costs low while retaining effectiveness. Lastly, the majority of training on equipment necessary to conduct these experiments and obtain results has been completed, including certification on the Gleeble, the arc melter, and electron microscopes.

60.3 Recent Progress

60.3.1 Acquired materials

One recent milestone for the project has been the arrival of initial materials that will be used for alloy fabrication, supplied by ATI Materials. The first shipment of materials included roughly 10 lbs. of Nb chips, a pound each of V chips, Hf chips, and Nb50Zr chips, as well as 2-3 lbs. of both Nb47Ti and Nb7.5Ta rod, as shown in **Figure 60.1**. These chip materials have all been cleaned and are ready for direct use in the arc melter once the machine has been verified to produce contaminant-free samples. Additional materials are scheduled for arrival within the coming month and include Ta chips, as well as alloy samples of Nb-Mo, Nb-W, and Nb-Re in varying concentrations. When the second shipment of material arrives, fabricating the initial round of binary alloy samples will commence.

60.3.2 Heat treatment plan

In addition to receiving some materials for alloy manufacturing, an initial draft heat treatment plan has been proposed, and input from industry is encouraged. Given the number of alloys planned, as well as independent variables introduced by deformation testing and heat treating, the heat treatment plan was designed to keep the final number of samples requiring EBSD analysis to a manageable amount. As such, all as-cast binary samples will undergo 60% reduction by hot rolling, with the baseline rolling reductions preformed at 500 ºC and 20% increments. Should a sample lack the workability to reach 60% deformation during this process, we will revise thermal-mechanical pathways or perhaps remove the alloy from consideration. Additionally, hardness tests will be conducted between each sequential step of the reduction process, allowing for later analysis of work hardening behavior.

Once the samples have been deformed and sectioned, they will be subjected to one of three heat treatment tests. Given that energy from cold work in most metals is stored below .3T_m and niobium has stable edge dislocations up to .5T_m [60.6], heat treatments for niobium should be conducted within this range. In industry, commercial practices for heat-treating niobium alloys intended for high temperature structural applications typically range from 1100-1300 ºC for a few hours [60.6], while heat treatments for the Nb3Sn formation take place between 600-800 ºC for on the order of 100 hrs [60.1, 60.3]. As such, the standard heat treatment temperature chosen was based around .4T_{mNb} (990 ºC) for an hour, as outlined in **Table 60.1** below. The second and third heat treatment will show how alloying effects vary with temperature and time respectively. ThermoCalc simulations were used to predict the theoretical melting temperatures of each binary, to inform the selection of a secondary heat treatment temperature. Binary alloys with predicted melting temperatures less than 2400 ºC will be treated at .42T_{mNb} (1050 ºC), greater than 2400 ºC but less than 2477 ºC will be treated at .43T_{mNb} (1075 ºC), and greater than 2477 ºC will be treated at .44T_{mNb} (1100 ºC). Table 60.1 is a simplified version of the current heat treatment plan, and while still subject to change, is in essence the current recrystallization testing plan for the initial round of binary alloy samples.

60.4 Plans for Next Reporting Period

Given the arrival of various raw materials and the proposed plans for thermal-mechanical processing and subsequent heat treating the initial binary alloy samples, the next steps for this project are as follows:

- Complete the casting of initial binary alloy samples using arc melter.
- Subject arc melted alloy samples to 60% reduction in rolling mill, and document changes in work hardening behavior.
- Section deformed samples into appropriate test specimens.
- Subject test specimens to heat treatment in the Gleeble or other furnace.
- Begin documenting microstructural evolution in test specimens using EBSD.
- Begin drafting testing plans for a second round of experiments.

60.5 References

[60.1] Balachandran, Shreyas, et al. "Beneficial influence of Hf and Zr additions to Nb4at% Ta on the vortex pinning of Nb3Sn with and without an O source." Superconductor Science and Technology 32.4 (2019): 044006.

[60.2] MagLab awarded $1.5m by U.S. Department of Energy to develop better superconductors. Florida State University News. (2020, July 20). Retrieved March 24, 2022, from https://news.fsu.edu/news/science-technology/2020/07/17/maglab-awarded-1-5m-by-u-s-department-of-energy-to-develop-better-superconductors/

[60.3] Banno, Nobuya, et al. "Influence of parent Nb-alloy grain morphology on the layer formation of Nb3Sn and its flux pinning characteristics." Scripta Materialia 199 (2021): 113822.

[60.4] Savitskii, 1970, Physical Metallurgy Of Refractory Metals and Alloys, Chapter 2, pp. 52

[60.5] Siciliano, F., Monteiro, W. A., & Padilha, A. F. (1995). Comparative study of the recrystallization of pure niobium and a NB-1 wt.% ZR alloy / Vergleichende Untersuchung des Rekristallisationsverhaltens von Reinem Niob und einer nb-1 Gew.‘ zr-legierung. International Journal of Materials Research, 86(10), 713–718. https://doi.org/10.1515/ijmr-1995-861010

[60.6] Wilkinson, W. D. (1969). Chapter 8. In Properties of refractory metals, Gordon and Breach Science, pp. 304–307.

60.5 Figures and Tables

Figure 60.1: The above picture shows the materials recently acquired for binary alloy manufacturing, supplied by ATI Materials. Contents include, Nb chips, Hf chips, V chips, Nb50Zr chips, Nb47Ti rod, and Nb7.5Ta rod. More materials are expected to arrive in the near future. Also pictured is the bucket they arrived in for scale.

Table 60.1: The table below is a simplified version of the initial heat treatment plan. Temperatures selected for heat treatment #2 are dependent on the theoretical melting temperature of the given alloy.

Sample: deformation	Nb-Ti 60%	Nb-Zr: 60%	Nb-Hf: 60%	Nb-V 60%	Nb: 60%	Nb-Ta: 60%	Nb-Mo 60%	Nb-W: 60%	Nb-Re: 60%
Heat treatment #1 (ºC; hrs)	990: 1	990: 1	990: 1	990: 1	990: 1	990: 1	990: 1	990: 1	990: 1
Heat treatment #2 (ºC; hrs)	1050: 1	1050: 1	1075: 1	1050: 1	1100: 1	1105: 1	1100: 1	1100: 1	1100: 1
Heat treatment #3 (ºC; hrs)	990: 2	990: 2	990: 2	990: 2	990: 2	990: 2	990: 2	990: 2	990: 2