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Comparative Study of the Recrystallization of Pure Niobium and a Nb–1 wt.% Zr Alloy

A comparative study on work hardening, recovery, recrystallization and grain growth of pure niobium and a Nb–1 wt.% Zr alloy has been carried out. Both materials were produced by electron beam melting. The deformation process (swaging) was the same for both materials. The degrees of deformation, which varied in the range 63 to 99 %, were calculated by the reduction in cross-sectional area. The annealing was performed in the following range of temperatures: 700 to 1300 °C for pure niobium and 800 to 1300 °C for the alloy. All the zirconium in the alloy was in solid solution, and the main effects of the zirconium addition were: solid solution hardening, increase of about 100 K in the temperatures of both start and end of recrystallization and strong inhibition of grain growth. Considerable softening was shown by both materials due to recovery processes.

Vergleichende Untersuchung des Rekristallisationsverhaltens von reinem Niob und einer Nb–1 Gew.% Zr-Legierung

Die Verfestigung durch Verformung, das Erholungs- und Rekristallistationsverhalten sowie das Kornwachstum von reinem Niob und einer Nb–1 Gew.% Zr-Legierung wurden vergleichend untersucht. Beide Werkstoffe wurden im Elektronenstrahlofen erschmolzen. Verformungsprozess (Rundhämmern) und Verformungsgrade waren für beide Werkstoffe identisch. Die Verformungsgrade, die im Bereich von 63 bis 99 % lagen, wurden aus der Querschnittsabnahme errechnet. Die Wärmebehandlung wurde bei 700 bis 1300 °C für Rein-Niob und 800 bis 1300 °C für die Legierung vorgenommen. Das gesamte Zirkonium der Legierung befand sich in fester Lösung (Mischkristall). Die Haupteinflüsse des Zirkoniumzusatzes waren: Mischkristallverfestigung, Erhöhung der Anfangs- und Endtemperatur der Rekristallisation um ungefähr 100 K und starke Hemmung des Kornwachstums. Beide Werkstoffe zeigten eine beachtliche Entfestigung während des Erholungsprozesses.

1 Introduction

Early techniques for the production of niobium relied on powder metallurgy processes that yielded impure materials with high concentration of interstitial elements. This problem was solved in the late fifties by remelting and refining the metal in electron beam furnaces.

The impurity levels presently attainable in niobium are much lower than they were by the time of the recrystallization studies of Page [1] and Begley and France [2]. Mechanical properties [3] and recrystallization temperature [4] are significantly affected by the interstitials O, N, C and H, which are the main impurities in niobium. In interstitial solution, the aforementioned elements induce asymmetric elastic strain fields in the niobium bcc lattice and, for this reason, interact strongly with dislocations, increasing hardness and reducing ductility. Substitutional solute atoms, like zirconium, exhibit a less pronounced interaction with crystalline defects and affect the ductility of niobium to a lesser extent than do the interstitials. However, similarly to the interstitials, zirconium increases the recrystallization temperature of niobium.

The deformation behavior of low impurity niobium and niobium alloys refined by electron beam melting has been reported by several investigators [1, 2, 5, 6]. It has been shown that the ductility of these materials is high and that they can be cold worked to 99 % reduction in cross-sectional area. Cellular dislocation structures have been reported to form in cold worked niobium specimens [7, 8]. Such behavior is typical for bcc metals with high stacking fault energy (SFE). Heterogeneities have also been observed in the microstructure of cold worked niobium, where the presence of deformation bands affected the recrystallization behavior.

Depending on the overall interstitial content and the heat treatment temperature, zirconium may be either in solid solution or in the form of oxides and carbides [5, 9 to 11]. Stewart et al. [5] have investigated the recrystallization of Nb–1 wt.% Zr and concluded that the presence of zirconium increases the recystallization temperature. The levels of both the interstitial and the substitutional impurities can affect the response of niobium and niobium alloys to work hardening, recovery, recrystallization and grain growth. Therefore, it is important to investigate these phenomena in materials with low impurity level.

This study was undertaken to investigate the work hardening, recovery, recrystallization and grain growth behavior of pure Nb and a Nb–1 wt.% Zr alloy. Both materials were produced by electron–beam melting and given the same amounts of deformation by rotary swaging. It was also the purpose of this work to investigate whether the zirconium in the alloy was present in solid solution or dispersed in the form of particles. The effects on the recrystallization temperature of both the zirconium addition and the amount of deformation were investigated over wide ranges of annealing temperatures and annealing times.

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Table 1. Interstitial content (ppm) in both materials.

	O	N	C
Nb	137	28	< 10
Nb–1 wt.% Zr	16	13	< 10

2 Materials and Experimental Procedure

The materials used in this work were obtained by aluminothermic reduction of Nb_2O_5, followed by melting and refining in an electron beam furnace. The Nb–1 wt.% Zr alloy was fabricated from electron beam refined niobium and pure zirconium. The resulting ingots were deformed to 26.5 mm diameter cylindrical bars. Oxygen, carbon and nitrogen contents of both materials are given in Table 1. The zirconium content of the alloy is presented in Table 2.

Table 2. Zirconium content in the alloy.

	WDS	atomic absorption spectroscopy
wt.% Zr	1.22	1.09

The 26.5 mm diameter cold worked bars were encapsulated in fused quartz tubes under vacuum of 1.0×10^{-5} torr and heat treated for 8 h at 1150 °C (pure niobium) and 1300 °C (Nb–1 wt.% Zr) to obtain a recrystallized microstructure. The recrystallized bars were then cold swaged to four levels of deformation, namely 63, 80, 92 and 99 % reduction in cross-sectional area. The deformed materials were encapsulated under vacuum and heat treated for 2, 4 and 6 h in the temperature range 700 to 1300 °C (pure niobium) and 800 to 1300 °C (Nb–1 wt.% Zr). The samples were not contaminated by atmospheric gases and the specimens were thick enough for the purpose.

Preparation of samples for metallographical observation consisted of mechanical grinding in SiC paper up to 600 mesh, followed by mechanical/chemical polishing with an abrasive composed of colloidal silica, ammonium hydroxide, distilled water, and hydrogen peroxide. All samples were etched with a solution of hydrofluoric acid, nitric acid and glycerin in the proportion 2:2:1, respectively.

Grain size determinations were made using the image analyser Quantimet Q-520, using 15 random fields for each recrystallized sample. Recrystallized fractions were determined by the point counting method using 20 random fields for each partially recrystallized specimen. Vickers microhardness was determined with a 0.2 kg load from at least seven indentations per sample.

TEM specimens of both materials were prepared by mechanically grinding samples down to 150 µm thickness followed by chemical thinning in a nitric acid solution containing 30 % hydrofluoric acid. Deformation heterogeneity and subgrain formation were investigated in pure niobium samples, and the presence of Zr-rich particles was investigated in alloy samples.

3 Results and Discussion

3.1 Characterization of the Starting Materials

An average grain diameter of 58.8 ± 29.9 µm was determined for the recrystallized niobium bar treated at 1150 °C for 8 h. The average grain size for the Nb–1 wt.% Zr bar treated at 1300 °C for 8 h was 55.3 ± 13 µm. Both materials were single-phase and free of precipitates. The occurrence of precipitates in Nb–1 wt.% Zr alloy with higher interstitial content than the alloy used in the present work has been reported in the literature [5, 11 to 13]. Figure 1 shows a precipitate-free microstructure in a Nb–1 wt.% Zr specimen.

Fig. 1. Bright field TEM image showing a microstructure free of precipitates in Nb–1 wt.% Zr alloy, after initial heat treatment.

3.2 Characterization of Deformed Materials

All specimens were easily deformed by cold swaging to high degrees of deformation. The observed high ductility is a result of the numerous slip systems of the bcc structure, the high SFE of niobium, and the low interstitial content of the samples. Figure 2 shows the effect of the amount of deformation by cold work on the microhardness of both the niobium and the Nb–1 wt.% Zr samples. Similar dependences are observed, suggesting that the presence of zirconium in solid solution has little effect on the SFE of niobium. However, solid solution hardening occurred due to solute–dislocation interaction. Figure 2 also suggests that both materials have similar work hardening rates.

3.3 Characterization of Annealed Materials

Three different types of deformed microstructures were annealed. The first type was unrecrystallized (NR), the second type was partially recrystallized (PR), and the third type was fully recrystallized (TR). Tables 3 and 4 show the results of the annealing treatments for both types of ma-

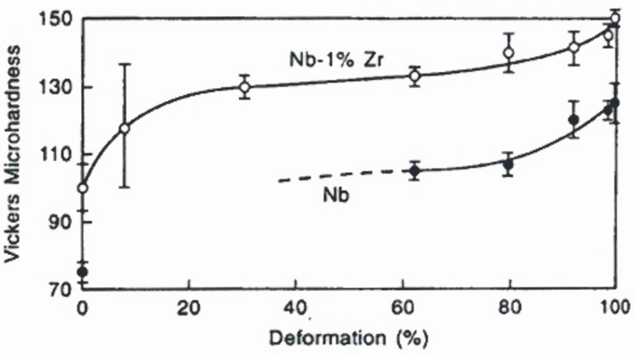

Fig. 2. Variation in Vickers microhardness (0.2 kg load) with the amount of cold deformation for both materials studied.

Table 3. Results for the annealed pure niobium specimens. For the non-recrystallized specimens (NR), the percentage of softening and the standard deviation are shown. For partially recrystallized specimens (PR) the fraction recrystallized (in %) and the standard deviation are shown. For totally recrystallized specimen (TR) the average grain size and the standard deviation are given.

Def (%)	Time (h)				Temperature (°C)			
		700	800	900	1000	1100	1200	1300
63.5	2			NR 25.5 ±26.4	PR 14.3 ±5.6	PR 69.4 ±19.4	TR 88.2 ±8.5	TR 562.9 ±68.3
	4			NR 24.3 ±27.3	PR 47.4 ±13.8	PR 88.2 ±18.3	TR 114.3 ±13.8	TR 818.3 ±88.6
	6			NR 31.3 ±17.3	PR 59.4 ±10.4	TR 50.3 ±6.8	TR 165.2 ±17.0	TR 1,199.8 ±253.4
79.7	2			PR 7.8 ±4.6	PR 55.8 ±17.2	TR 35.3 ±5.3	TR 86.1 ±6.3	TR 569.8 ±50.9
	4			PR 15.8 ±5.5	PR 70.3 ±25.2	TR 41.0 ±6.2	TR 113.0 ±9.1	TR 806.3 ±61.1
	6			PR 21.8 ±7.2	PR 84.7 ±10.6	TR 42.3 ±7.5	TR 155.3 ±19.9	TR 1,207.1 ±202.7
92.3	2		NR 23.5 ±8.0	PR 23.9 ±10.2	TR 32.0 ±10.0	TR 35.2 ±16.2	TR 78.2 ±4.8	TR 609.4 ±42.9
	4		NR 29.5 ±4.8	PR 40.7 ±10.4	TR 33.0 ±11.9	TR 43.9 ±16.1	TR 117.3 ±11.8	TR 919.4 ±85.3
	6		NR 30.5 ±11.3	PR 51.2 ±16.6	TR 34.5 ±8.5	TR 43.3 ±13.3	TR 175.0 ±15.3	TR 1,274.5 ±164.0
98.6	2	NR 37.7 ±9.1	PR 9.6 ±4.2	PR 49.0 ±10.4	TR 16.8 ±2.5	TR 24.2 ±2.1	TR 83.0 ±3.6	TR 743.1 ±37.6
	4	NR 40.5 ±9.3	PR 24.4 ±8.2	PR 64.6 ±9.6	TR 18.1 ±2.1	TR 25.3 ±3.0	TR 107.8 ±8.1	TR 1,024.4 ±86.5
	6	NR 40.8 ±10.2	PR 38.0 ±13.6	PR 72.6 ±10.4	TR 21.3 ±1.4	TR 28.2 ±3.5	TR 186.6 ±18.6	TR 1,267.4 ±137.8

terials, according to the type of microstructure. The data are presented as percentage of softening for unrecrystallized samples, fraction recrystallized for partially recrystallized samples, and average grain size in the case of fully recrystallized samples.

3.3.1 Unrecrystallized Specimens (NR)

The unrecrystallized specimens of niobium and Nb–1 wt.% Zr showed considerable softening due to recovery processes. The amount of softening (S) of a sample X was calculated as

$$S = \frac{Hw - Hx}{Hw - Hr} \times 100$$

where Hw and Hr are the hardness in the cold worked and recrystallized conditions, respectively, and Hx is the hardness measured on the specimen X.

The significant amounts of softening shown in Tables 3 and 4 are attributed to the high SFE of the materials, which allows crystalline defects, mainly dislocations, to rearrange and partially annihilate, reducing the driving force for recrystallization. The pure niobium specimens with the highest and lowest degree of deformation did not recrystallize after 6 h at temperatures below 700 and 900 °C, respectively. The correspondent temperatures for Nb–1 wt.% Zr samples were 800 and 1000 °C. The increase of 100 °C in the temperature for the start of recrystallization of Nb–1 wt.% Zr samples is attributed to the presence of zirconium atoms in solid solution. Zirconium may affect the movement and rearrangement of dislocations, delaying the start of recrystallization. For the same reason, the evolution of softening with time was more evident for the niobium specimens. Dragging forces on dislocations due to the zirconium atoms might have been responsible for the indistinct evolution of the amount of softening, as well as for the high dispersion of the results from the Nb–1 wt.% Zr samples.

3.3.2 Partially Recrystallized Specimens (PR)

Partial recrystallization of the niobium samples was found to occur between 800 and 900 °C in the specimens with the highest degree of deformation and between 1000 and 1100 °C in the specimens with the lowest degree of deformation. The difference in the temperature for the start of recrystallization in the two materials studied is attributed to the zirconium addition, which slows down the recovery

Table 4. Results for the annealed Nb–1 wt.%Zr specimens. For the non-recrystallized specimens (NR), the percentage of softening and the standard deviation are shown. For partially recrystallized specimens (PR) the fraction recrystallized (in %) and the standard deviation are shown. For totally recrystallized specimen (TR) the average grain size and the standard deviation are given.

Def (%)	Time (h)	Temperature (°C) 800	900	1000	1100	1200	1300
61.2	2		NR 27.5 ±11.3	NR 35.1 ±13.2	PR 3.2 ±2.7	PR 76.0 ±11.2	TR 60.8 ±9.7
	4		NR 28.3 ±16.3	NR 27.6 ±22.4	PR 7.1 ±5.4	TR 37.2 ±3.9	TR 63.2 ±7.3
	6		NR 26.0 ±14.5	NR 24.7 ±20.1	PR 8.9 ±5.6	TR 56.7 ±3.8	TR 71.0 ±11.6
78.4	2		NR 34.6 ±8.8	NR 35.7 ±14.9	PR 37.2 ±23.1	TR 29.5 ±2.0	TR 42.1 ±6.5
	4		NR 28.7 ±20.3	PR 17.9 ±11.7	PR 50.6 ±24.5	TR 34.4 ±3.8	TR 46.3 ±4.9
	6		NR 36.5 ±15.8	PR 15.4 ±9.8	PR 54.9 ±21.2	TR 39.7 ±3.6	TR 48.2 ±3.2
91.2	2		NR 40.4 ±14.1	PR 11.9 ±4.3	PR 46.9 ±8.2	TR 26.6 ±2.4	TR 37.1 ±2.3
	4		NR 28.0 ±15.5	PR 17.5 ±5.7	PR 61.2 ±9.6	TR 28.4 ±3.3	TR 42.0 ±3.5
	6		NR 31.1 ±12.6	PR 19.9 ±7.1	PR 74.3 ±16.7	TR 31.2 ±2.7	TR 48.7 ±4.5
98.5	2	NR 21.4 ±4.8	NR 40.9 ±10.5	PR 22.3 ±7.2	PR 69.6 ±9.6	TR 24.7 ±2.3	TR 30.0 ±1.6
	4	NR 24.8 ±13.4	NR 50.9 ±7.8	PR 32.1 ±8.2	PR 87.6 ±11.1	TR 25.9 ±2.8	TR 40.6 ±3.4
	6	NR 26.1 ±7.2	PR 10.7 ±4.4	PR 34.7 ±11.7	PR 86.5 ±12.0	TR 27.2 ±2.0	TR 44.1 ±6.8

kinetics. Since the beginning of recrystallization (nucleation) in highly deformed specimens consists of recovery phenomena such as subgrain coalescence and subgrain growth, the formation of recrystallized nuclei was probably retarded by the presence of zirconium in solid solution.

The difference of 100 °C observed in the temperatures for the end of recrystallization in the two materials investigated may be related to two factors:

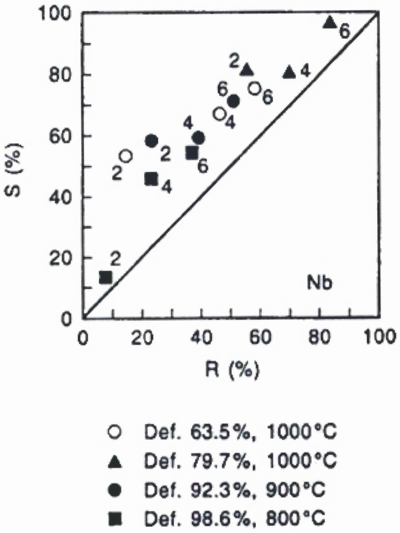

Fig. 3. (left) Relation between the softened fraction (S) and the recrystallized fraction (R) for pure niobium specimens.

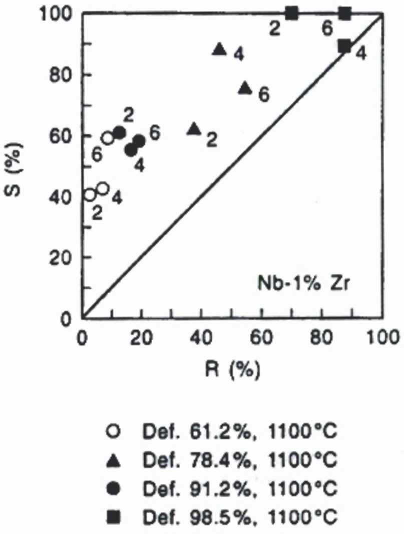

Fig. 4. (right) Relation between the softened fraction (S) and the recrystallized fraction (R) for Nb–1 wt.% Zr alloy specimens.

Fig. 5. Evolution of the recrystallized fraction in Nb specimens. (a) Deformed by 79.7 % and treated at 900 °C for 2 h; (b) deformed by 92.3 % and treated at 900 °C for 6 h; (c) deformed by 79.7 % and treated at 1000 °C for 6 h (for recrystallized fractions see Tables 3 and 4).

(i) In the alloy, the temperature for the start of recrystallization is higher because zirconium in solid solution interacts with dislocations during the recovery processes;

(ii) Dragging forces on high-angle grain boundaries due to the presence of zirconium in solid solution may decrease boundary mobility. This is suggested by the faster increase of the recrystallized fraction in pure niobium samples relative to that of alloy samples.

Figures 3 and 4 show the relation between softened and recrystallized fractions for pure niobium and alloy samples, respectively. They show that in partially recrystallized samples of both materials, the softened fraction was always larger than the recrystallized fraction. Numbers within the figures represent the annealing time in hours for the pair deformation-temperature. Both figures indicate that the occurrence of significant amounts of recovery decreased the driving force for grain boundary migration. Previous works [15 to 18] have shown that recovery processes play an important role at low recrystallization temperatures, after small deformations and for high SFE metals.

Figure 5 shows examples of partially recrystallized microstructures in pure niobium specimens. Recrystallized nuclei could not be identified by optical microscopy in specimens deformed by 98.6 % and annealed for up to 6 h at 700 °C. However, previous investigators [6 to 8] have reported the occurrence of recrystallization in pure niobium at temperatures of 700 °C and lower for annealing times shorter than 6 h. In those cases, the total interstitial content was always less than 115 ppm and recrystallized nuclei were observed by transmission electron microscopy [7, 8]. In addition, the deformation processes and heating rates were different from those employed in the present investigation. In this study, fully recrystallized specimens were not obtained at temperatures below 700 °C even after 100 h annealing time. The occurrence of recovery, which lowers the driving force for recrystallization, and the insufficient thermal activation for high-angle grain boundary migration were probably the factors responsible for the incomplete recrystallization at low annealing temperatures.

Additional annealing experiments were performed at 700 and 800 °C for 100 h on pure niobium specimens deformed by 98.6 %. These experiments resulted in partially recrystallized microstructures, as observed by optical microscopy. Such microstructures are shown in Fig. 6. Long anneals did not lead to fully recrystallized specimens because the low SFE of niobium facilitated the occurrence of recovery, which, in turn, lowered the driving force for recrystallization.

3.3.3 Fully Recrystallized Specimens (TR)

The TR specimens exhibited a wide range of grain sizes. The smallest grain sizes were found in specimens with the highest amount of deformation annealed for short times at low temperatures. The influence of the amount of deformation, time and temperature agreed with the "laws of recrystallization" of Burke and Turnbull [19].

Pure niobium specimens showed grain sizes in the range of 16.7 to 1267.4 μm. For the annealing times used in this work, the niobium specimens with the highest and lowest amounts of deformation became fully recrystallized at temperatures of 1000 °C or higher and 1100 °C, respectively. Significant grain growth was not observed at those temperatures. However, at 1200 and 1300 °C, considerable variation of grain size was found. It is difficult to explain the presence of grain diameters larger than 1 mm due to normal grain growth. On the other hand, secondary recrystallization is not likely to occur due to the following reasons: First, a bimodal grain size distribution was not observed in TR specimens. Although some heterogeneities were found, they did not seem sufficient to promote abnormal grain growth. Second, a particle dispersion was not observed in

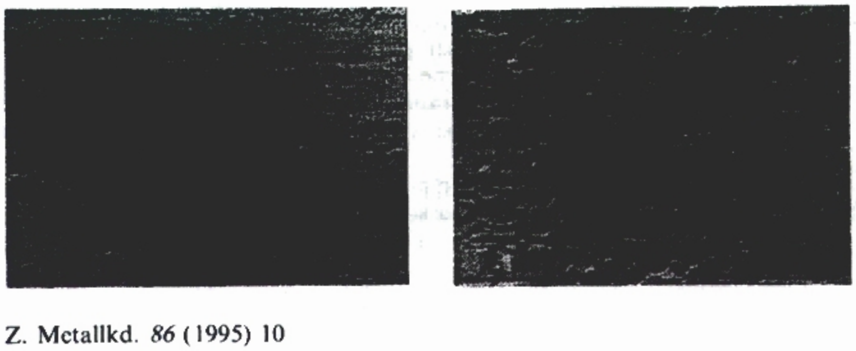

Fig. 6. Partially recrystallized microstructures of niobium specimens deformed by 98.6 % and treated for 100 h at (a) 700 °C; (b) 800 °C.

both materials. Therefore, it is not possible to rule out the occurrence of secondary recrystallization based solely on the results of the present experiments, and additional work is required for this purpose.

For the Nb–1 wt.% Zr specimens, fully recrystallized microstructures were observed at temperatures of 1200 °C or higher, depending on the amount of previous cold work. The grain size of these specimens varied from 24.7 to 71 μm. The presence of zirconium in solid solution strongly inhibited grain growth. The dragging force on high-angle boundaries due to the zirconium atoms was very effective in preventing grain growth, as suggested by the driving force for grain growth, which was about 100 times lower than the driving force for recrystallization.

4 Conclusions

The following conclusions can be drawn from the experiments carried out in this work:

- The presence of particles and inclusions has not been detected in both materials studied.
- The presence of 1 wt.% zirconium in solid solution caused a considerable hardening but did not change the work hardening rate of the niobium.
- Both materials showed considerable recovery before and during the occurrence of recrystallization.
- The presence of 1 wt.% zirconium in solid solution raised the temperatures of start and end of recrystallization by about 100 °C.
- The presence of 1 wt.% zirconium in solid solution had a strong inhibition effect on grain growth.

From a technological point of view, the experiments performed permitted the following conclusions:

- The deformation by swaging enabled the materials to be easily deformed by up to 99 % (reduction in area).
- The results of this work permit thermo-mechanical treatments which produce a wide range of microstructures. It is also possible to obtain small grain sizes (17 to 25 μm: ASTM 8 to 7 approximately) in both materials tested.
- The risk of obtaining huge grain sizes is higher for pure niobium than for Nb–1 wt.% Zr alloy.

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