NASA TECHNICAL NOTE

NASA TN D-7847

NASA TN D-7847

HARDNESS BEHAVIOR OF BINARY AND TERNARY NIOBIUM ALLOYS AT 77 AND 300 K

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • DECEMBER 1974

1. Report No. NASA TN D-7847	2. Government Accession No.	3. Recipient's Catalog No.

4. Title and Subtitle

HARDNESS BEHAVIOR OF BINARY AND TERNARY NIOBIUM ALLOYS AT 77 AND 300 K

5. Report Date
December 1974

6. Performing Organization Code

7. Author(s)
Joseph R. Stephens and Walter R. Witzke

8. Performing Organization Report No.
E-8083

9. Performing Organization Name and Address

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio 44135

10. Work Unit No.
506-16

11. Contract or Grant No.

12. Sponsoring Agency Name and Address

National Aeronautics and Space Administration
Washington, D.C. 20546

13. Type of Report and Period Covered
Technical Note

14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

An investigation was conducted to determine the effects of alloy additions of zirconium, hafnium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, and iridium on the hardness of niobium. Both binary and ternary alloys were investigated by means of hardness tests at 77 and 300 K. Results showed that atomic size misfit plays a dominant role in controlling hardness of binary niobium alloys. Alloy softening, which occurred at dilute solute additions, is most likely due to an extrinsic mechanism involving interaction between solute elements and interstitial impurities.

17. Key Words (Suggested by Author(s))		18. Distribution Statement
Hardness	Alloy softening	Unclassified - unlimited
Niobium alloys	Atomic size misfit	Category 17

19. Security Classif. (of this report)	20. Security Classif. (of this page)	21. No. of Pages	22. Price*
Unclassified	Unclassified	14	$3.25

* For sale by the National Technical Information Service, Springfield, Virginia 22151

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SUMMARY

An investigation was conducted to determine the effects of alloy additions of zirconium, hafnium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, and iridium on the hardness behavior of niobium (Nb). Both binary and ternary alloys were investigated by means of hardness tests at 77 and 300 K, or within the temperature range where alloy softening is normally observed in body-centered-cubic metals. Alloys were prepared by arc melting high-purity electron-beam-melted niobium and high-purity alloying elements. Alloy additions ranged from less than 1 atomic percent up to the maximum solubility of each of the elements in Nb, or up to 30 to 40 atomic percent solute for those elements that are completely soluble in Nb.

Results showed that atomic size misfit plays a dominant role in controlling hardness in the binary alloy systems investigated. Alloy hardening was observed at 300 K for all solute contents, and hardness data could be correlated with the square root of solute content. At 77 K reasonably good agreement was observed with a similar correlation. Hardness at 77 K was erratic at low solute contents. When the hardness of arc-melted Nb was used as a baseline, alloy softening was observed at 77 K with dilute solute additions. However, when the hardness of an ultra-high-vacuum, high-temperature annealed specimen was used as a baseline, only alloy hardening was observed at 77 K in the Nb alloys. Softening in Nb alloys at 77 K probably arises from a solute-interstitial interaction, as suggested by others. This type of softening and the role of atomic size misfit in Nb alloys is quite different from the softening and the role of electron concentration in controlling hardness in binary molybdenum (Mo) alloys, which suggests a basic difference in softening and hardening behavior between body-centered-cubic group V (Nb) and group VI (Mo) alloys.

INTRODUCTION

Alloy softening in body-centered-cubic (bcc) alloys has been studied extensively by numerous investigators over the past few years. Although softening observed in group V and group VI metal systems and softening in iron have many similar characteristics, there is still disagreement as to the mechanisms that produce softening in bcc alloys.

Recent results obtained by the authors showed that alloy softening occurs in the group VI metals, chromium (Cr), molybdenum (Mo), and tungsten (W), as the result of the addition of solute elements that have an excess of s and d electrons compared with the group VI metals (refs. 1 and 2). It was further shown that softening and hardening in Mo alloys could be correlated with the number of s and d electrons contributed by the solute elements. Thus, the authors suggest that an intrinsic mechanism controls the hardness of group VI metal alloys.

Alloy softening has also been observed in group V metals, vanadium (V), niobium (Nb), and tantalum (Ta) (refs. 3 to 5). However, alloy softening exhibited by as-grown single-crystal Ta-rhenium (Re) alloys (ref. 6) at 77 K was not present at 77 K after the same specimens were heated in an ultra-high-vacuum system at a temperature near the melting point (ref. 7). A comparison of the data indicated that the strength of unalloyed Ta was markedly reduced after the ultra-high-vacuum anneal, apparently because of removal of interstitial impurities. In contrast, the Ta-Re alloy crystals exhibited an increase in strength as a result of the annealing treatment. A similar observation of ultra-high-vacuum annealing resulting in reduced strength has been reported for unalloyed Nb (ref. 8). These results are cited as evidence that an extrinsic mechanism such as solute-interstitial interaction is responsible for alloy softening in Ta and Nb alloys. However, there still remains considerable disagreement concerning alloy softening in group V alloys, with several other investigators (refs. 3 and 4) attributing softening to an intrinsic mechanism such as lowering of the Peierls stress.

Most of the previous studies on group V alloys have involved only one or two alloy systems. A more extensive study of several alloy systems such as the one the authors conducted on binary Mo alloys (ref. 2) has not been performed on any of the group V metals. In addition, the previous studies have not correlated the softening or strengthening results with such parameters as atom size misfit or modulus as has been done for face-centered-cubic (fcc) alloys (ref. 9).

The purpose of the present investigation was twofold: (1) to characterize the hardness behavior of binary and ternary Nb-base alloys containing solute additions which have fewer or more s and d electrons than Nb to determine if alloy softening occurs in these alloys, and (2) to identify the major factor or factors controlling the hardness of Nb alloys.

Niobium alloys investigated included binaries with additions of zirconium (Zr), hafnium (Hf), Mo, W, Re, ruthenium (Ru), osmium (Os), rhodium (Rh), and iridium (Ir) plus ternary Nb alloys from the Nb-Hf-Mo system. A total of 55 binary and ternary Nb alloys were investigated. Hardness was measured at 77 and 300 K, which correspond to homologous temperatures of 0.03 and 0.11 T_m (where T_m is the melting temperature), that is, within the homologous temperature range where alloy softening is normally observed in bcc alloys.

EXPERIMENT

Materials

Materials for this investigation included high-purity electron-beam-melted Nb, Mo, W, Re, and Zr; commercial-purity Hf turnings; and hydrogen-annealed Ru, Os, Rh, and Ir powders. Ingots were prepared by nonconsumable triple arc melting of 70-gram charges in a water-cooled copper mold, followed by drop casting into a square-cross-section mold. A portion of the arc-melted, unalloyed Nb specimen was heated in an ultra-high-vacuum furnace at about 0.9 T_m for approximately 14 hours to reduce the interstitial-impurity content of the specimen. The annealing was performed at Case Western Reserve University.

Table I presents the analyzed compositions of the binary and ternary Nb alloys. Interstitial analyses of several alloys from each alloy series are also listed in table I. Because of the limited specimen size, interstitial analysis could not be obtained on the ultra-high-vacuum-annealed specimen. A typical analysis obtained on single-crystal specimens heat treated under similar conditions is given in table I.

Slices, approximately 3 millimeters thick and 15 millimeters on a side, were cut from the cast ingots for hardness testing. One face of each specimen that was to be used for hardness testing was given a metallographic polish. Specimens were then annealed in vacuum for 1 hour at 0.7 T_m or at a higher temperature within the solid solution range in order to reduce segregation and produce single-phase, equiaxed, strain-free specimens.

Apparatus

The modified microhardness test unit used in this study has been described previously (ref. 1). The test unit permitted hardness measurements at 77 K as well as 300 K.

Procedure

Alloying elements for binary Nb alloys were selected from the fifth and sixth periods of the periodic table and consisted of Zr and Hf, which have fewer s and d electrons than Nb, and Mo, W, Re, Ru, Os, Rh, and Ir, which have more s and d electrons than Nb. Ternary alloy additions to Nb consisted of Hf and Mo. Concentrations of binary solutes normally extended over the solubility range or up to 30 or 40 atom percent solute in those systems where total solubility exists.

Test temperatures for Nb alloys were 77 and 300 K or 0.03 and 0.11 $T_{m, Nb}$. At least 10 diamond pyramid hardness impressions were made on each alloy at each of the two test temperatures. A load of 1 kilogram and a dwell time of 15 seconds were used for the impressions. The relative standard deviation was 5 percent.

Lattice parameter measurements were made on Nb-Os alloys by using standard diffractometer techniques.

RESULTS

Solute Effects

Hardness data for Nb alloys are summarized in table I. The hardness behavior of binary Nb alloys at 77 K is illustrated in figure 1(a). Attention should be drawn to the hardness of unalloyed Nb, for which two values are plotted in figure 1(a). The higher value, 208, is for an arc-melted button prepared for this study, while the lower value, 171, is for part of the same specimen after it was annealed in an ultra-high-vacuum system. As indicated in table I and reported previously (ref. 8), this annealing treatment dramatically reduces interstitial-impurity levels in Nb and thus lowers the hardness, as illustrated in figure 1(a). Hardness tests on an ultra-high-vacuum-annealed single-crystal Nb specimen gave hardness values similar to those obtained for the arc-melted annealed polycrystalline specimen and thus indicated similar purity. When the annealed material is used as a baseline, it can be noted that only alloy hardening is observed (see inset in fig. 1(a)) in the nine binary alloy systems investigated. Figure 1(a) further indicates that hardening rate increases with increasing group number of the solute elements; however, no correlation was found between hardness and s and d electrons for Nb-base alloys. Based on the strength of zone-melted and of outgassed Nb single crystals, it has been suggested that softening in Nb and probably in the other group V metals, V and Ta, is due to interaction of solutes and interstitial impurities (ref. 10).

Figure 1(b) shows similar hardness behavior at 300 K for the binary Nb alloys. Again, the hardness of unalloyed Nb is reduced, from 74 to 38, as a result of the high-vacuum, high-temperature anneal, and alloy softening is not observed at this test temperature with either hardness value for Nb. Hardening rates observed for these alloy systems again increase with increasing group number, as was observed at 77 K.

Figure 2 shows the hardness behavior of ternary Nb-Hf-Mo alloys at 77 and 300 K. The hardness varies linearly with total solute content at both test temperatures over a total solute content range of 10 to approximately 40 atomic percent. For Hf-Mo additions to Nb, hardening is additive over a large range of solute additions.

Since the type of softening reported previously for Nb-W alloys (ref. 4) and observed in Mo alloys (ref. 2) at solute contents of 4 to 8 atomic percent was not observed in Nb alloys at 77 or 300 K, hardness was not investigated at other temperatures for the binary or ternary alloys.

Figure 3 is a correlation of the hardness of binary Nb alloys with the square root of solute content that is similar to the correlations reported for fcc alloys (ref. 9). In figure 3(a) reasonably good agreement is shown for data at 77 K for most of the alloy systems. A probable cause of the erratic hardness behavior in some systems (e.g., in the Nb-Hf system) is variations in interstitial contents, which apparently have a marked effect on hardness at this temperature. The Nb-Re data could not be correlated with square root of solute content. In contrast, at 300 K the correlation was good for all systems, as shown in figure 3(b).

Size Effects

An analysis of the data indicated that electron concentration did not play a major role in controlling the hardness of the nine Nb-base alloy systems investigated in this study. Therefore, an attempt was made to correlate the observed hardening rates with atomic size misfits. Figure 4 shows the effect of solute additions on the lattice parameter of Nb as reported by Pearson (ref. 11) for all the alloy systems except Nb-Os, which has not been treated in the literature. Measurements were made on specimens from this study to obtain the data shown in figure 4 for Nb-Os alloys. It should be noted that Zr and Hf, which have fewer s and d electrons than Nb, produce an increase in the lattice parameter upon alloying in Nb. The remaining seven elements, which have more s and d electrons than Nb, all result in a decrease in lattice parameter upon alloying with Nb. The calculations of atomic radius by Teatum, Gschneider, and Waber (ref. 12) indicate that Hf and Zr have larger atomic radii than Nb, while the remaining seven elements have smaller atomic radii than Nb, which is in agreement with the change in lattice parameters.

In figure 5, the change in hardness with the square root of solute content $dH/dc^{1/2}$ at 300 K, from figure 3(b), is plotted against the change in lattice parameter with solute content da/dc, from figure 4. Lattice parameters were not available for 77 K; therefore, a plot of $dH/dc^{1/2}$ against da/dc could not be made for this temperature. Hardening in Nb-base alloys can be correlated with lattice-parameter changes, which indicates that atomic size misfit plays a dominant role in controlling the low-temperature hardness of Nb-base alloys. This is in contrast to the group VI metals, Cr, Mo, and W, for which the authors have shown (refs. 1 and 2) that electron concentration plays the dominant role in controlling hardness.

It also should be noted in figure 5 that Hf and Mo additions to Nb produce similar hardening rates. This may explain why a simple additive relation between hardness and total solute content was observed for Nb-Hf-Mo ternary alloys. Combinations involving Hf with Os or other elements with quite different hardening rates might lead to a much more complex relation between hardness and solute content for ternary alloys.

DISCUSSION

It was determined that hardening rates of group V Nb alloys could be correlated with change in lattice parameter, which suggests that atomic size misfit plays the dominant role in controlling hardness of Nb alloys. Similar observations have been reported for fcc alloys (ref. 10), where both atomic size misfit and modulus mismatch were shown to be important. Attempts were made to correlate the hardness of binary Nb alloys with electron concentration; however, no general equation could describe the data from the nine alloy systems investigated. Hardening rate did appear to increase with increasing group number of the solute elements; however, it is concluded that this trend plays at most a minor role in controlling the hardness of Nb alloys.

Correlation of hardness of Nb (group V) alloys with atomic size misfit rather than electron concentration, as was done for Mo (group VI) alloys, suggests a basic difference in the low-temperature deformation of the two groups of bcc metals. The group V metals exhibit several similarities to fcc metals which include (1) correlation of hardness with atomic size misfit, and (2) good low-temperature ductility with an absence of a ductile-brittle transition temperature in metal of high purity. Although the low-temperature ($<0.2\ T_m$) deformation behavior of bcc group V and group VI metals is generally treated as a whole (ref. 9), the present results, along with the work of others (refs. 13 and 14), suggest that both physical and mechanical properties for the two groups can be quite different. Chen (ref. 13) in a review of the physical properties of the two groups has proposed a subdivision of the bcc metals, based on differences in the electronic structure and nuclear composition, between group V (V, Nb, and Ta) and group VI (Cr, Mo, and W). Chen concludes that systematic differences in many physical properties between groups are manifestations of this subdivision and that mechanical properties may be expected to show a marked difference in behavior. More recently Taylor, Vessely, and Christian (ref. 14) have shown basic differences in the low-temperature slip behavior for the two groups of bcc metals.

When the hardness of high-temperature, ultra-high-vacuum-annealed Nb was used as a baseline, alloy softening was not observed in this study. When the higher hardness, arc-melted Nb was used as a baseline, alloy softening was observed at 77 K, but only at very dilute concentrations of solutes. Softening observed in Nb appears to be associated with an extrinsic property, interaction of solute elements and interstitial impurities, as suggested by Ravi and Gibala (refs. 8 and 10). This type of softening is quite different from that observed for group VI metals, where an intrinsic mechanism related to electron concentration is believed to control the hardness behavior. Thus, alloy softening is further support for a subdivision of the bcc transition metals by group, group V and group VI.

CONCLUSIONS

A study of the hardness behavior of niobium alloys containing solute additions of zirconium, hafnium, molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, and iridium has yielded the following conclusions:

1. Atomic size of solute elements plays the major role in controlling the hardness of niobium alloys. Electron concentration plays a minimal role, if any, in controlling hardness of niobium alloys.
2. Alloy softening in niobium, which can occur at very dilute solute contents in arc-melted material, is most likely due to solute-interstitial interactions, as suggested by others. Alloy softening can be eliminated by ultra-high-vacuum annealing, which reduces interstitial-impurity content.
3. Alloy hardening in ternary niobium-hafnium-molybdenum alloys is additive and varies linearly with total amount of solute.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, October 3, 1974,
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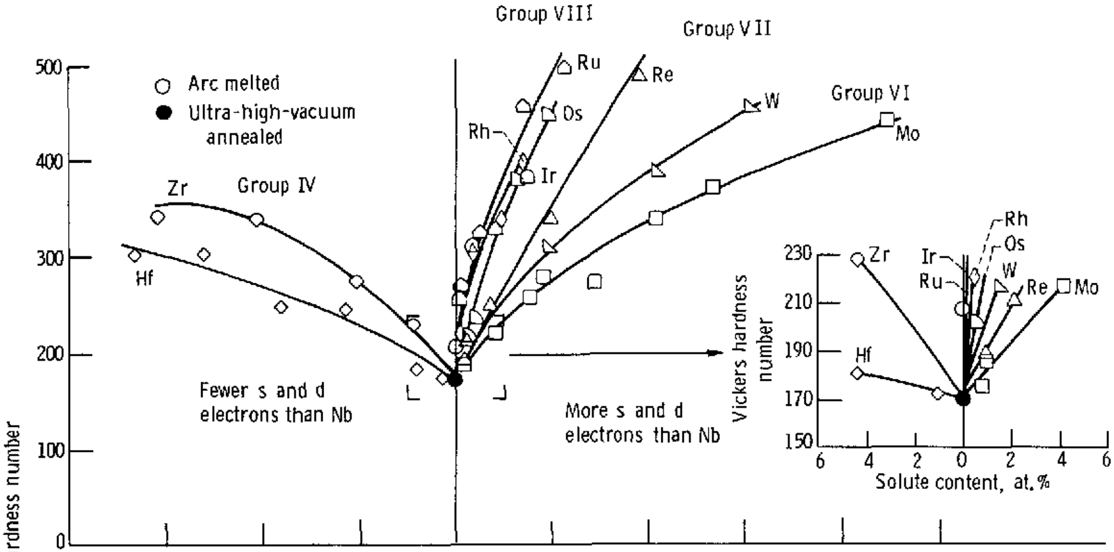
TABLE 1. - CHEMICAL ANALYSIS AND SUMMARY OF HARDNESS DATA FOR NIOBIUM AND BINARY AND TERNARY NIOBIUM ALLOYS

Solute	Analyzed solute content, at. %	Analyzed interstitial content, ppm by wt.			Temperature, K	
		Carbon	Oxygen	Nitrogen	77	300
					Vickers hardness number	
Niobium						
None	(a)	70	38	62	208	74
	(b)	---	---	---	171	38
	(c)	6	10	1	---	35
Binary alloys						
Zirconium	4.3	---	---	---	229	148
	10.1	18	64	141	273	193
	20.5	---	---	---	339	251
	30.6	21	94	138	342	287
Hafnium	0.99	---	---	---	173	89
	4.2	---	---	---	181	117
	11.3	---	212	72	248	178
	17.9	32	106	66	248	189
	25.8	19	148	54	303	230
	33.1	---	86	4	303	240
Molybdenum	0.82	---	---	76	175	88
	1.0	---	191	---	185	99
	4.2	24	110	80	217	136
	7.9	35	185	96	254	171
	9.2	33	177	94	276	175
	15.5	20	118	78	272	222
	21.0	---	228	72	335	259
	27.0	26	142	68	368	302
	44.7	---	52	28	435	353
Tungsten	1.5	116	70	220	216	131
	9.6	---	---	---	307	201
	21.0	56	118	146	383	256
	30.7	48	124	100	448	321
Rhenium	1.0	---	---	---	188	99
	2.2	36	94	97	211	127
	4.0	---	---	---	247	158
	10.4	40	106	98	337	260
	19.5	54	42	42	482	380
Ruthenium	0.63	---	---	---	268	148
	2.8	39	233	169	324	168
	7.5	---	---	---	453	265
	11.8	16	100	77	495	341
Osmium	0.56	---	---	---	203	122
	2.3	28	228	175	259	182
	6.5	---	---	---	377	280
	9.9	16	150	162	445	326
Rhodium	0.53	---	---	---	221	106
	2.0	123	136	120	297	143
	5.0	---	---	---	334	211
	7.2	36	107	123	395	254
Iridium	0.49	---	---	---	254	116
	2.0	58	206	138	309	158
	5.0	---	---	---	325	226
	7.6	24	144	82	381	272
Ternary alloys						
Hafnium, molybdenum	5.3, 5.0	42	272	98	235	176
	5.2, 9.6	---	100	78	286	214
	5.1, 19.4	---	106	74	344	277
	10.1, 5.1	---	105	76	291	206
	9.8, 9.8	26	110	63	314	245
	10.1, 19.5	---	109	55	373	309
	10.0, 27.4	---	255	110	469	371
	20.3, 4.9	---	198	77	320	254
	20.1, 9.0	22	77	56	377	307

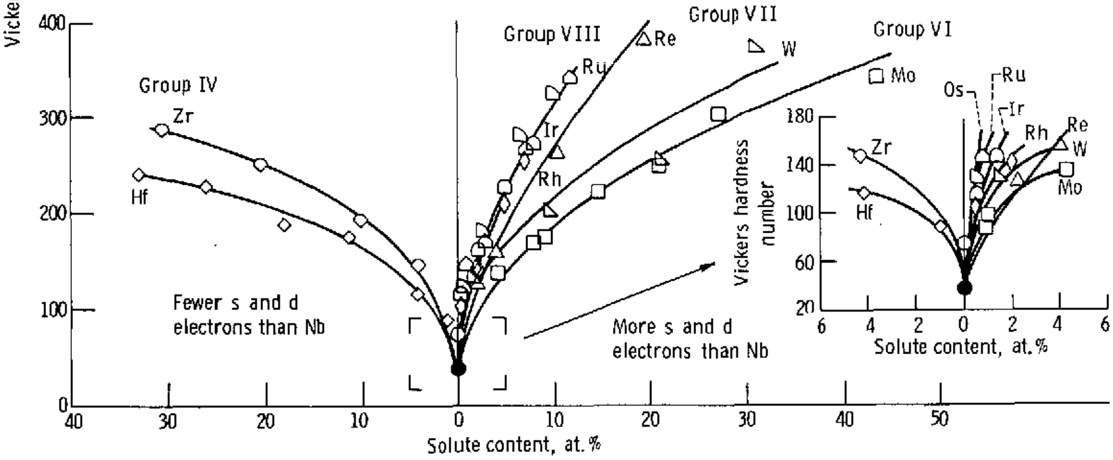
[a] Arc-melted Nb.

[b] Polycrystalline Nb, annealed in ultrahigh vacuum at about 0.9 T_m.

[c] Zone-refined Nb single crystal, also ultra-high-vacuum annealed.



(a) 77 K.



(b) 300 K.

Figure 1. - Effect of solute content on hardness of binary niobium alloys.

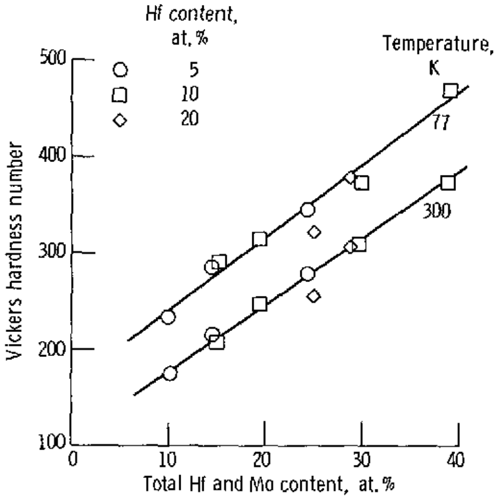
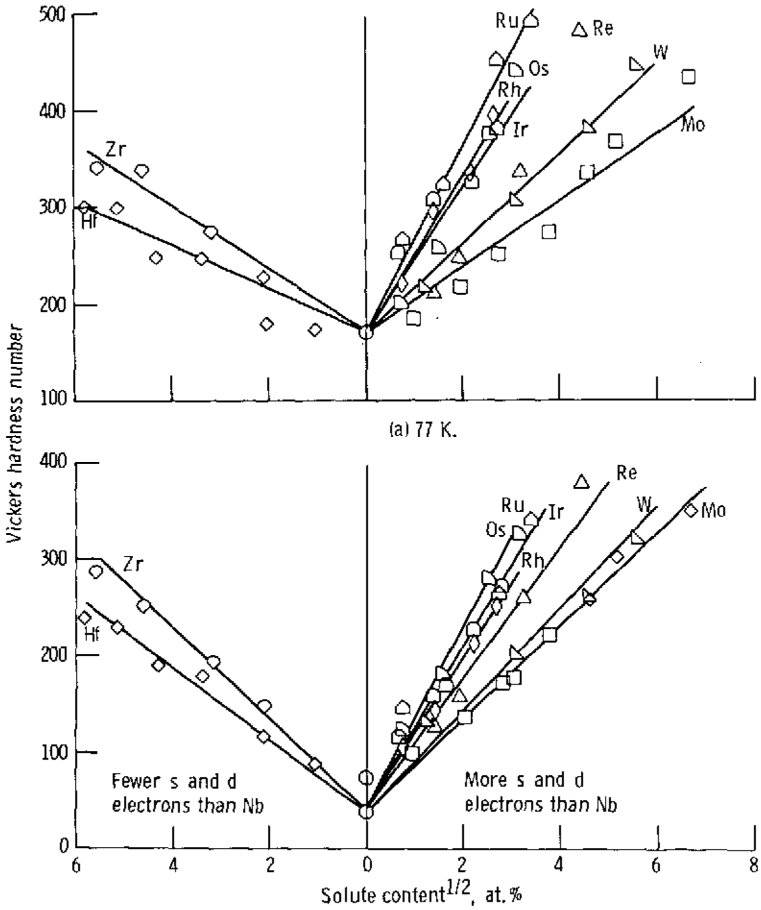


Figure 2. - Hardness behavior of ternary niobium-hafnium-molybdenum alloys.



(a) 77 K.

(b) 300 K.

Figure 3. - Correlation of hardness of niobium alloys with square root of solute content.

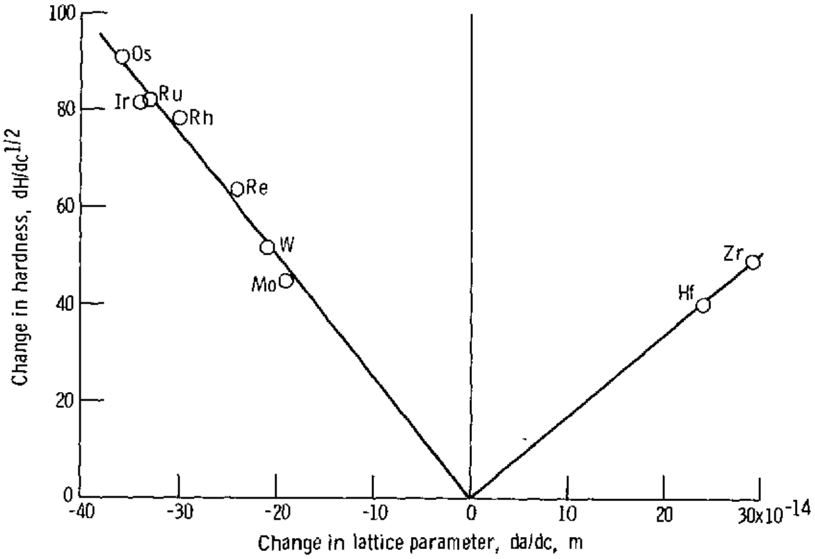


Figure 5. - Correlation of hardening rates of binary niobium alloys with change in lattice parameter at 300 K.

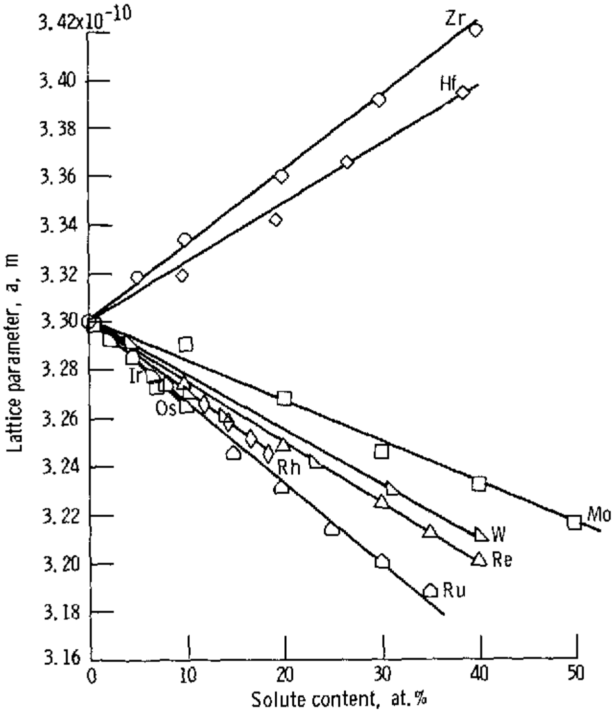


Figure 4. - Effect of solute content on lattice parameter of niobium. (Osmium data from this investigation; all other data from ref. 11.)

NASA-Langley, 1974