

AN ABSTRACT OF THE THESIS OF

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A series of TiNbHf alloys ranging from 0-40 atomic % Nb and 0-15 atomic % Hf were evaluated to investigate low-elastic modulus phenomena which occur in this ternary system. The desirability of utilizing corrosion-resistant, biocompatible alloys with elastic modulus values approaching that of human bone for medical prosthetic implants provides an incentive for this work.

Data are presented in this report which indicate that Ti alloys containing approximately 10 atomic % Nb and 1-6 atomic % Hf may be solution-heat-treated to obtain modulus values approximately 25% that of steel and 50% that of titanium. The quenched alloys may subsequently be precipitation-hardened to attain yield strengths of 125-130 Kpsi while retaining low-elastic moduli.

Characterization of TiNbHf Alloys for Potential
Medical/Dental Applications

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Darryl D. Amick

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Professor of Materials Science in Charge of Major

Redacted for Privacy

Head of Department of Mechanical Engineering

Redacted for Privacy

Dean of the Graduate School

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Typed by Nancy Mickelberry for Darryl D. Amick

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CHARACTERIZATION OF TiNbHf ALLOYS FOR POTENTIAL MEDICAL/DENTAL APPLICATIONS

I. INTRODUCTION

Materials utilized for orthopedic implants must perform a wide variety of functions, many of which may be quite unfamiliar to the materials scientist. Whereas factors such as corrosion resistance may normally be viewed from the standpoint of the effect of the environment on the material, biomaterials must also consider the effect of the material upon the environment (i.e., the human body).¹ Considerations of such biological factors as toxicity, carcinogenicity, allergenicity, mutagenicity, etc., take the materials scientist far afield from his normal area of expertise and make it imperative that appropriate input be obtained from biological professionals.

Even well-established, traditional implant materials face continual and intensified scrutiny as more knowledge is gained by the medical community. Metallic alloys such as stainless steel, CoCr, and Ti6Al4V have recently come under criticism for either proven or perceived problems involving the release of metallic ions into the human body, some of which are suspected of having long-term, as well as short-term, undesirable effects. In fact, only

five metallic elements have been identified as producing no adverse tissue reactions in the human body.² These elements are niobium, tantalum, titanium, zirconium, and platinum. A new alloy, Ti13Zr13Nb (wt. %), has recently been developed and proposed for use in total hip replacement (THR) and total knee replacement (TKR) surgery. Not only does this alloy address the concerns of potential tissue reaction, but it also may be heat treated to obtain relatively high yield strength (750 MPa) with remarkably low Young's modulus (80 GPa). The latter property is important in avoiding "stress shielding" and accompanying bone "resorption" which are discussed in detail later in this paper.

In considering the five approved elements referred to above, it is observed that vanadium (Group V A), other noble metals of the platinum group, and hafnium (Group IV A) are conspicuously absent. While one may dismiss the Pt group metals as perhaps too expensive to justify obtaining approval for implants, vanadium has been shown to be potentially toxic, leaving hafnium for further consideration. Hf appears to be an element for which biocompatibility has not been established simply because of insufficient data, rather than because of any negative findings. Chemical and physical considerations indicate that Hf should be expected to be at least as innocuous in biological environments as the other Group IV A elements,

Ti and Zr. This paper also illustrates that Hf, as an alloy element in TiNb alloys, may be superior to Zr toward increasing yield strength and decreasing Young's modulus. Although Hf is not presently approved as a human implantation material, the excellent oxidation resistance, corrosion resistance in a wide variety of media, and high stability of oxides, nitrides, carbides and other compounds of this element make it an attractive candidate for such applications.

An ideal implant for major bone replacement should have tensile yield strength similar to that of Ti6Al4V (800 MPa/116 Kpsi, minimum), elastic modulus as low as possible (approaching that of bone: 31 GPa/4.5 Mpsi), excellent corrosion resistance and relatively low density, in addition to other biological requirements discussed herein.

As the field of orthopedic implants is large and diverse, this report will place emphasis on one particular application: the total hip replacement prosthesis. It should be understood, however, that the subject alloys may be useful in other orthopedics and dental applications involving hard tissue repair and/or replacement.

II. BACKGROUND/LITERATURE SURVEY

In reviewing the literature addressing metallic orthopedic implants, it is evident that a wide variety of material and design selections have been utilized, some of which reflect a lack of metallurgical knowledge. For example, even common steel nails have been employed as bone fixation devices, with the predictable result that severe rusting has occurred. Other examples involve the indiscriminate mixing of components such as screws and pins made of different alloys.³ This practice resulted in galvanic corrosion of the more anodic components as would be expected of dissimilar metals in the presence of an electrolyte (i.e., body fluids). Such corrosion is not only detrimental from the standpoint of reduced strength in the prosthesis, but also from release of corrosion products (metallic ions and inorganic debris) into the human body. An example of this is the attachment of stainless steel pins with tantalum screws in repairing a severely broken radius bone. (The patient, ironically, was a metallurgist.) The result was severe pain and eventual destruction of the radius which was ultimately removed in its entirety.⁴ Other cases point to the fact that intimate contact of the dissimilar metals is not necessary for galvanic corrosion to occur. It is sufficient to merely locate such materials in the same local region of the body.³

In addressing corrosion, which may include not only galvanic but also crevice erosion/corrosion, direct oxidation, chemical dissolution and stress-corrosion types, the materials scientist is confronted with complex problems in how to design meaningful testing procedures. Although it is practically impossible to apply *in vitro* results to *in vivo* performance, laboratory results may be effectively used to rank materials in relation to each other.¹ Such comparisons have played a role in the evolution of materials selection preferences beginning with the discontinued utilization of vanadium steels developed specifically for human implants, and their replacement by 302 stainless steel (old designation "18-8"). This alloy in turn was modified by the addition of molybdenum to improve corrosion resistance in saline solutions, and eventually came to be classified as type 316 SS, which was itself modified by lowering carbon content to increase corrosion resistance in chloride solutions. The resulting stainless steel grade (316L) finds wide usage as an implant alloy.⁵

Further ranking by means of both *in vitro* and *in vivo* corrosion evaluations has shown that corrosion resistance increases in the order of 316L, Co-Cr alloys, and Ti6Al4V, all of which are presently widely utilized for implants.⁶ Another means of ranking materials, and perhaps a more meaningful one, is to study

electrochemical effects on biocompatibility, as determined by actual healing in human bone.⁷ When current densities in a fast-reacting redox system, $K_4[Fe(CN)_6]/K_3[Fe(CN)_6]$ were measured, gold was highest, followed by stainless steel, Co-Cr, and Ti6Al4V.¹ The same order was noted in observing the degree of disturbance in the initial bone healing process; i.e., gold interfered with healing to the greatest degree, while Ti6Al4V caused very little interference.⁸ The explanation which has been offered for these results is that surface oxides apparently serve to prevent the exchange of electrons and thereby suppress redox reactions at the implant surface.¹ (It is not known why the electrical currents generated by corrosion processes interfere with bone healing.) To imply that simple corrosion resistance is always the primary concern in selecting materials for implants, however, would be misleading. All of the alloys mentioned above owe their corrosion resistance to the presence of protective oxide films which serve as barriers to further diffusion of a variety of chemical species.⁹ Destruction of these protective films by, for example, mechanical abrasion and the ease with which films reform are critical factors.

It has been demonstrated that there is a transition from corrosion control to electron exchange control of polarization resistance during spontaneous passivation of

film-forming alloys.¹ An extremely complex series of transient conditions may therefore be encountered when abrasive wear and subsequent reformation of the passivating film are considered. Abrasion may not only degrade corrosion resistance but may also result in deposition of debris in joints. This is the primary reason that Co-Cr alloys are presently utilized for knee joint prostheses, whereas Ti6Al4V may be superior in hip joint replacements which do not involve such severe shear/abrasion stresses.¹⁰ Because of the need to simultaneously consider corrosion resistance and wear resistance, it may sometimes be preferable to dismiss the philosophy that dissimilar metals should not be allowed to contact each other.¹¹⁻¹⁴ For example, it was recently felt to be desirable to fabricate the femoral ball in a hip prosthesis from wear-resistant Co-Cr and attach it to a Ti6Al4V femoral stem. While corrosion was observed at the ball-stem interface, it was later observed that the same phenomenon occurred when Co-Cr balls and stems were similarly joined mechanically, especially when one component was cast and the other wrought. This same type of corrosion has been observed in ball\stem assemblies in which both components were Ti6Al4V, leading to the conclusion that a mechanical factor may be important in initiating the observed crevice corrosion. Accordingly, it is now deemed to be important to achieve extremely close dimensional matching between the ball and stem.¹

Aside from corrosion and abrasion, a major consideration in orthopedic implants is the method by which the prosthesis is attached to the bone. In the case of the total hip replacement, several methods for attaching the ball/stem assembly to the remaining segment of the femur have been utilized.³ In the late 1950s bone cements based on PMMA (polymethylmethacrylate) were introduced and have been used with great success.¹⁵ This polymer cement serves as a shock absorber as it has visco-elastic properties.³ The THR operation achieved such great success in elderly patients that increasingly younger patients sought the procedure. The increased performance criteria associated with younger, more active people were not adequately provided by the cemented prosthesis, resulting in loosening of bonded interfaces. This in turn resulted in excessive pain and often actual mechanical failure of the prosthesis. Because of this problem, a trend has developed toward the use of cementless, interference fit methods which have become recently popular.² The primary problem associated with this approach, "stress shielding", is one which may be effectively approached by the materials engineering community.

Viewing the human femur from the front or rear, a significant curvature (concave downward) is noted as the bone deviates from the generally straight lower segment of the femur toward the hip socket.¹⁶ In a normal bone,

the body's weight tends to flex this region so that the curvature increases as weight is shifted to that side of the body. The Young's elastic modulus of cortical bone is about 31 GPa (4.5 Mpsi), far below values for common engineering alloys.¹⁷ When a relatively stiff prosthesis is inserted into the intramedullary canal of the femur, the curved region in question may become "shielded" from flexural stresses.¹⁶ As is true of other biological structures (e.g., muscles), the absence of stress and flexure may result in a form of atrophication. In the specific case of bone "shielding", the body resorbs and weakens the bone, which may ultimately cause loosening or fracture of the prosthetic stem.¹⁸ Attempts to design the prosthesis so that the curved region of the femur experiences increased stresses by increasing the length of the curved neck have created excessive moments at other points, causing fractures.³ A logical approach to this problem would appear to be to develop suitable alloys with lower elastic modulus values, while preserving adequate strength, corrosion resistance and other required attributes. Recognizing this potential, various researchers have presented the following information, which tends to encourage further development of such alloys.

Significant reductions in bone resorption have been demonstrated in dogs and sheep with low modulus hip

implants.¹⁹⁻²³ Finite element analyses have confirmed that healthy femurs are more closely simulated by low modulus materials.²⁴ Strain gauge¹ analyses have also confirmed this finding.²⁵⁻²⁹ In human patients, bone resorption,²² loosening,³⁰ and the pain which has clearly been attributed to excessive prosthetic stiffness has been shown to be reduced in frequency and severity by using low modulus hips.³¹⁻³³ Metallic materials are felt to be preferable to other materials, such as polymer composites, because of cost considerations and the poor wear resistance of these composites.

A major medical prosthetics producer, Smith and Nephew/Richards Medical, has worked with a reactive/refractory metals producer, Teledyne Wah Chang Albany, in developing a Ti13Zr13Nb (wt. %) low-modulus alloy.² This alloy appears to have an advantage over other new low-modulus alloys in that it contains only elements which have been demonstrated to have no adverse tissue reactions. The other alloys referred to include Ti5Al2.5Fe, Ti6Al7Nb ("Protasul-100") and Ti11.5Mo6Zr2Fe (TMZF"). The first two of these still have relatively high modulus (105-115 GPa versus 120 GPa for Ti6Al4V) and contain the potentially undesirable element aluminum. TMZF contains relatively high concentrations of Mo and Fe, both of which have been demonstrated to cause severe tissue reactions.

The candidacy of TiNb alloys as low modulus materials is not surprising when a review of Ti alloy literature is conducted. A large body of work has been documented as a result of research in metallic superconductors.³⁴ Whereas the present "workhorse" alloy of this industry is Nb47Ti (wt. %), a vast amount of earlier research was conducted in ZrNb alloys as well. Notable in both these and other binary systems involving Ti alloyed with other transition metals (TM) is the significant effect of electron/atom ratio on elastic modulus and other physical and mechanical properties. In the cases of Ti-Mo, Ti-Nb, and Ti-V, for example, a minimum value for Young's modulus occurs at 4.1 e/a with another (although not as prominent) minimum at slightly higher values. These anomalies are attributable to martensitic transformations which occur upon rapidly quenching the alloys from temperatures above the α - β transformation to temperatures at which the equilibrium structure would be α -HCP. In pure Ti, Zr and Hf (and dilute Ti-TM alloys) the transformation structure is HCP while other Ti-TM alloys transform to a martensitic orthorhombic structure. In alloys such as TiNb, it is possible to follow the solution-treat-and-quench operation by precipitating second-phase particles in the two-phase ($\alpha + \beta$) region of the binary-phase diagram. As may be observed in the respective binary-phase diagrams of Nb, Zr, or Hf in Ti,³⁵ these three elements tend to act as "beta

stabilizers", lowering the α - β transformation temperature from its pure (Ti) value of 882°C. It is possible to control the precipitation process so as to obtain sub-microscopic second-phase particles.² Significant strengthening is observed (as presented later in this report), indicating a high degree of coherency between these particles and the matrix structure.

III. EXPERIMENTAL PROCEDURES

The experiments involved in developing the subject TiNbHf alloys were conducted in several stages, the results of initial experiments providing a basis for subsequent work. For this reason, the report is presented with reference to the following two phases:

- 1) Determination of the elastic modulus as a function of composition for a range of TiNbHf alloys.
- 2) Characterization of alloys with minimum elastic modulus values.

A. Phase I - Elastic Modulus as a Function of Composition

After referring to a published plot of elastic modulus versus atomic % Nb in Ti (Figure 1), a series of sixteen Ti alloys containing 4-38 at.% Nb and 5-15 at.% Hf were prepared by vacuum-arc melting Ti sponge (Kroll), Hf sponge (Kroll), and Nb turnings in a water-cooled copper crucible to produce alloy buttons of approximately 400 grams. Table 1 presents the sixteen different compositions prepared, along with specimens of pure Ti and Ti_{7.75}Nb_{7.8}Zr, at.% (an experimental alloy presently under evaluation by other researchers) which were included for comparison.

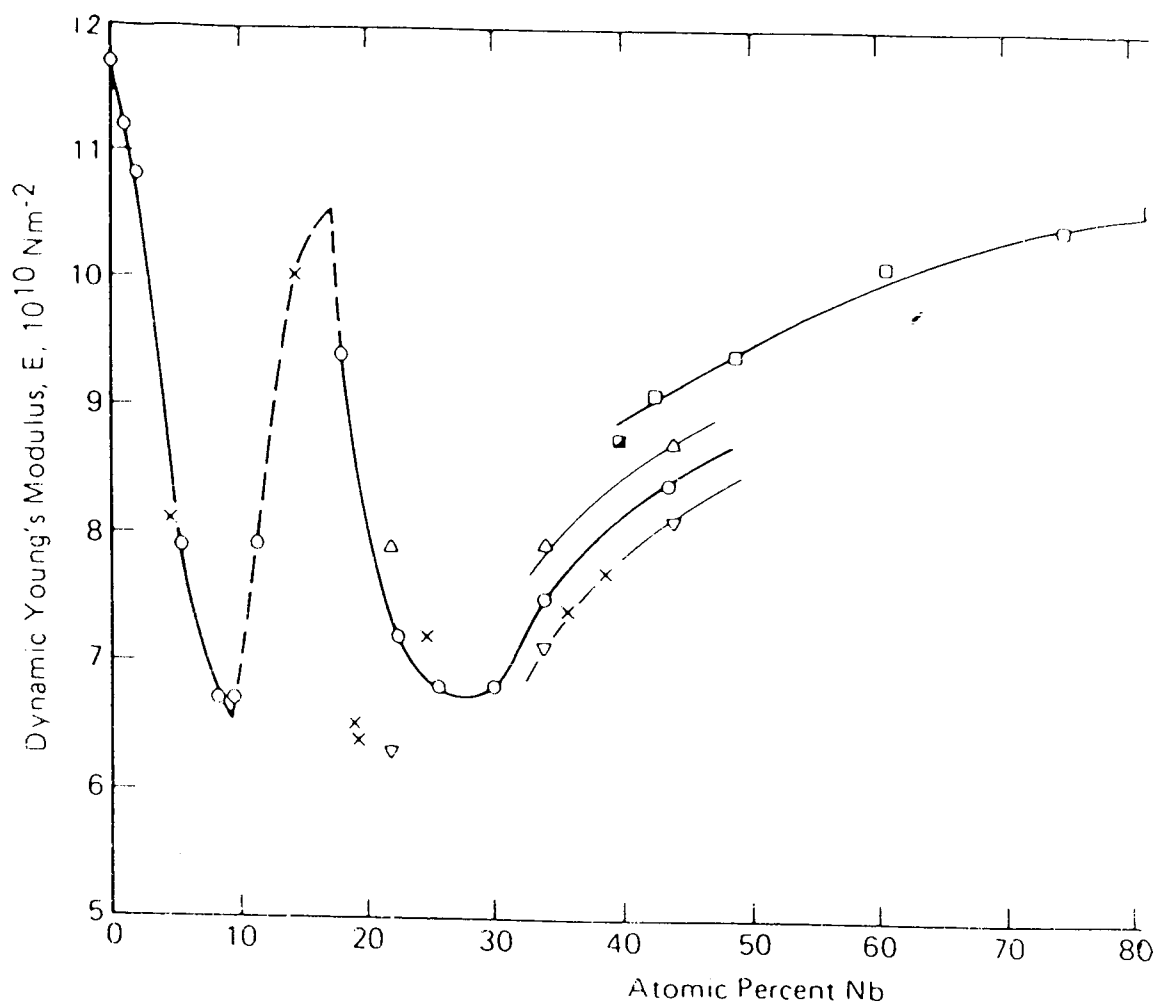


Figure 1. Modulus vs. Atomic % Nb in Ti (from Applied Superconductivity - Metallurgy and Physics of Titanium Alloys, Vol. 1, p. 201. W. E. Collings, author; Plenum Press, publisher, 1985).

Note: Data represents solution-treated-and-quenched samples evaluated by various researchers.

TABLE 1. TiNbHf COMPOSITIONS - PHASE I

Alloy	Atomic Ratio		Atomic Z			Weight Z			e/a
	Ti:Nb	Nb/ Nb+Ti	Ti	Nb	Hf	Ti	Nb	Hf	
1	∞	0	100	--	--	100	--	--	4.0
2	20	4.74	90.5	4.5	5.0	76.8	7.4	15.8	4.05
3	10	9.05	86.4	8.6	5.0	71.0	13.7	15.3	4.08
4	5	16.63	79.2	15.8	5.0	61.65	23.85	14.5	4.16
5	3	25.05	71.2	23.8	5.0	52.4	33.9	13.7	4.24
6	1.5	40.0	57.0	38.0	5.0	38.2	49.3	12.5	4.38
7	20	4.78	85.7	4.3	10.0	65.3	6.3	28.4	4.04
8	10	9.11	81.8	8.2	10.0	60.6	11.8	27.6	4.08
9	5	16.67	75.0	15.0	10.0	53.0	20.6	26.4	4.15
10	3	25.0	67.5	22.5	10.0	45.5	29.4	25.1	4.22
11	1.5	40.0	54.0	36.0	10.0	33.5	43.4	23.1	4.35
12	20	4.71	81.0	4.0	15.0	56.0	5.4	38.6	4.04
13	10	9.06	77.3	7.7	15.0	52.2	10.0	37.8	4.08
14	5	16.71	70.8	14.2	15.0	45.9	17.9	36.2	4.14
15	3	25.0	63.75	21.25	15.0	39.6	25.6	34.8	4.21
16	1.5	40.0	51.0	34.0	15.0	29.5	38.2	32.3	4.34
17	10.91	8.4	84.55	7.75	7.8	65.7	11.7	22.6	4.08
18	10.91	8.4	84.55	7.75	7.8 Zr no Hf	74	13	13 Zr no Hf	4.08

Following a homogenizing heat treatment in vacuum for 2.0 hours at 1500°C, samples of the as-cast specimens were removed. The remaining portions of all eighteen buttons were hot rolled from 850°C to approximately 3.0 mm thick. Overall reduction in thickness was 75%, attained by six passes of approximately 20% per pass. No reheating was performed during this rolling sequence.

Specimens were then heated to 850°C, held at-temperature for 30 minutes, and quenched into water at 20°C. After removing samples representing the as-quenched condition, other specimens of each alloy were exposed to 500°C for aging times of 1, 2, 3, 4, 5 and 6 hours, elastic modulus values being measured after each hour increment of aging time.

Determinations of Young's modulus were made by utilizing a Grind-o-Sonic® instrument which indirectly measures modulus by evaluating vibrational characteristics of mechanically stimulated specimens. This method is referred to as "impulse response analysis" (IRA). This method allowed the same sample to be measured after successive increments of aging time in a very convenient manner. Modulus measurements were taken on all as-cast, quenched, and aged specimens, the pure Ti specimen serving as a calibration standard for each condition.

Densities for each specimen at each condition were determined as a necessary part of the Young's modulus calculation.

Young's modulus values for the as-quenched specimens were plotted and compared against published values for binary TiNb alloys of this same condition.

B. Phase II - Characterization of Alloys with Minimum Elastic Modulus Values

As detailed in the Phase I Results section of this report, plots of Young's modulus versus Nb content for alloys containing 5, 10, and 15 at.% Hf were found to display minima at approximately 10 and 30 at.% Nb. These results, in conjunction with published data for binary NbTi alloys,³⁴ suggested a more thorough evaluation of alloys containing 1-6 at.% Hf at Nb concentrations of 10 and 40 at.% Nb. Accordingly, buttons of 16 different alloy compositions (Table 2) were prepared in the manner described in Phase I.

Included in these experiments were two binary TiNb alloys (10 and 40 at.% Nb), as well as the Ti7.75 Nb7.8Zr alloy and its Hf-containing counterpart Ti7.75Nb7.8Hf. A minor change in input material was made, in that Nb55 wt.% Ti rather than pure Nb turnings were used to the

TABLE 2. TiNbHf COMPOSITIONS - PHASE II

Alloy No.	Atomic %			Weight %			Constituent Weights (400 g)			
	Ti	Nb	Hf	Ti	Nb	Hf	Ti	Nb	Nb47Ti	Hf
19	60	40	0	43.6	56.4	0	0	28.94	371.06	0
20	90	10	0	82.3	17.7	0	266.4	0	133.58	0
21	56.4	37.6	6	37.18	48.08	14.74	7.72	33.32	300	58.96
22	84.6	9.4	6	67.58	14.56	17.86	218.67	0	109.89	71.44
23	57	38	5	38.17	49.35	12.48	11.68	38.4	300	49.92
24	85.5	9.5	5	69.76	15.03	15.21	225.72	0	113.43	60.84
25	57.6	38.4	4	39.19	50.67	10.14	0	25.91	333.53	40.56
26	86.4	9.6	4	72.05	15.53	12.43	233.11	0	117.21	49.72
27	58.2	38.8	3	40.43	52.27	7.77	0	26.71	344.08	31.08
28	87.3	9.7	3	74.43	16.04	9.53	240.82	0	121.06	38.12
29	58.8	39.2	2	41.33	53.43	5.24	0	27.29	351.74	20.96
30	88.2	9.8	2	76.92	16.58	6.50	248.87	0	125.13	26.0
31	59.4	39.6	1	42.45	54.89	2.66	0	28.08	361.28	10.64
32	89.1	9.9	1	79.53	17.14	3.33	257.32	0	129.36	13.32
33	84.55	7.75	7.8	65.72	11.68	22.59	221.45	0	88.15	90.36
34	84.55	7.75	0 (7.8Zr)	73.88	13.13	(12.98Zr)	248.95	0	99.09	51.92 (Zr)

extent allowable as the source of Nb. This precaution was taken to minimize the possibility of Nb-rich inclusions, indications of which had been observed in Phase I buttons.

Buttons were homogenized for 2.0 hours at 1500°C, machined to a uniform thickness of 7.5 mm and X-radiographed to confirm the absence of unalloyed inclusions.

Hot rolling at 850°C was also conducted in a more conservative manner by reheating at the completion of each rolling pass. In rolling from 7.5 mm to 3.0 mm, four 20% reductions in thickness were required.

Water quenching from 850°C (1.0 hour soak) was followed by aging at 500°C for times of 0.5, 1.5, 2.5, 4, and 6 hours. Young's modulus and density values were determined for all as-cast, as-rolled, as-quenched and aged samples.

Following IRA modulus testing, the six-hour-aged specimens were sheared in half lengthwise, and each resulting piece was again measured for modulus to determine variability of the material and testing procedure. One piece (identified as "A") from each set was submitted for tensile testing in the aged condition. Remaining pieces ("B") were reprocessed by heating for one hour at

850°C, followed by water quenching. This procedure was utilized to determine reproducibility of the original as-quenched modulus readings. After obtaining IRA modulus measurements, these pieces were also submitted for tensile testing of the as-quenched condition. Metallographic specimens were cut and prepared, from which micro-structural and microhardness data were obtained.

IV. RESULTS

A. PHASE I

Measured as-cast densities of the eighteen alloys are presented in Table 3, which also reorganizes chemical composition in terms of atomic ratios for convenience in plotting subsequent graphs.

Young's modulus values determined by IRA for as-cast and as-quenched conditions are presented in Table 4.

Effects of Nb and Hf concentrations on Young's modulus are illustrated graphically in Figures 2 and 3 for as-cast and as-quenched conditions, respectively. Included in Figure 3 for purposes of comparison is a plot for the binary TiNb alloy obtained from published data. It is apparent that both binary and Hf-containing alloys exhibit minima at approximately 10 and 30 atomic % Nb after quenching.

The effect of aging quenched specimens for times of 1-6 hours at 500°C on Young's modulus is presented in Table 5 and in Figures 4-7. The latter three figures are plots of Young's modulus versus aging time, and include curves for pure Ti and for reference alloys #17 and #18.

TABLE 3. COMPOSITION VS. DENSITY

Alloy	Atomic %			Weight %			Atomic Ratio		Density g/cm ³
	Ti	Nb	Hf	Ti	Nb	Hf	Ti:Nb	Nb/(Nb+Ti)	
1	100	--	--	100	--	--	∞	0	4.597
2	90.5	4.5	5.0	76.8	7.4	15.8	20	4.74	5.286
3	86.4	8.6	5.0	71.0	13.7	15.3	10	9.05	5.487
4	79.2	15.8	5.0	61.65	23.85	14.5	5	16.63	5.792
5	71.2	23.8	5.0	52.4	33.9	13.7	3	25.05	6.060
6	57.0	38.0	5.0	38.2	49.3	12.5	1.5	40.0	6.804
7	85.7	4.3	10.0	65.3	6.3	28.4	20	4.78	5.818
8	81.8	8.2	10.0	60.6	11.8	27.6	10	9.11	5.963
9	75.0	15.0	10.0	53.0	20.6	26.4	5	16.67	6.297
10	67.5	22.5	10.0	45.5	29.4	25.1	3	25.0	6.518
11	54.0	36.0	10.0	33.5	43.4	23.1	1.5	40.0	7.134
12	81.0	4.0	15.0	56.0	5.4	38.6	20	4.71	6.291
13	77.3	7.7	15.0	52.2	10.0	37.8	10	9.06	6.504
14	70.8	14.2	15.0	45.9	17.9	36.2	5	16.71	6.931
15	63.75	21.25	15.0	39.6	25.6	34.8	3	25.0	7.109
16	51.0	34.0	15.0	29.5	38.2	32.3	1.5	40.0	7.600
17	84.55	7.75	7.8	65.7	11.7	22.6	10.91	8.4	5.752
18	84.55	7.75	7.8 Zr no Hf	74	13	13 Zr No Hf	10.91	8.4	5.214

TABLE 4. YOUNG'S MODULUS VALUES

ALLOY NO.	AS-CAST MODULUS, GPa	* ROLLED, HEAT-TREATED MODULUS, GPa
1	113.0	103.4
2	97.9	87.5
3	81.3	54.7
4	102.0	77.2
5	72.4	59.5
6	83.4	79.9
7	98.6	82.7
8	85.4	63.7
9	101.3	75.1
10	78.6	66.1
11	85.4	95.8
12	98.6	88.9
13	86.1	71.0
14	104.8	73.0
15	81.3	68.3
16	85.4	97.2
17	91.0	64.2
18	87.5	67.3

* As-cast samples were hot-rolled at 850°C, reheated to 850° for 30 minutes, and water quenched.

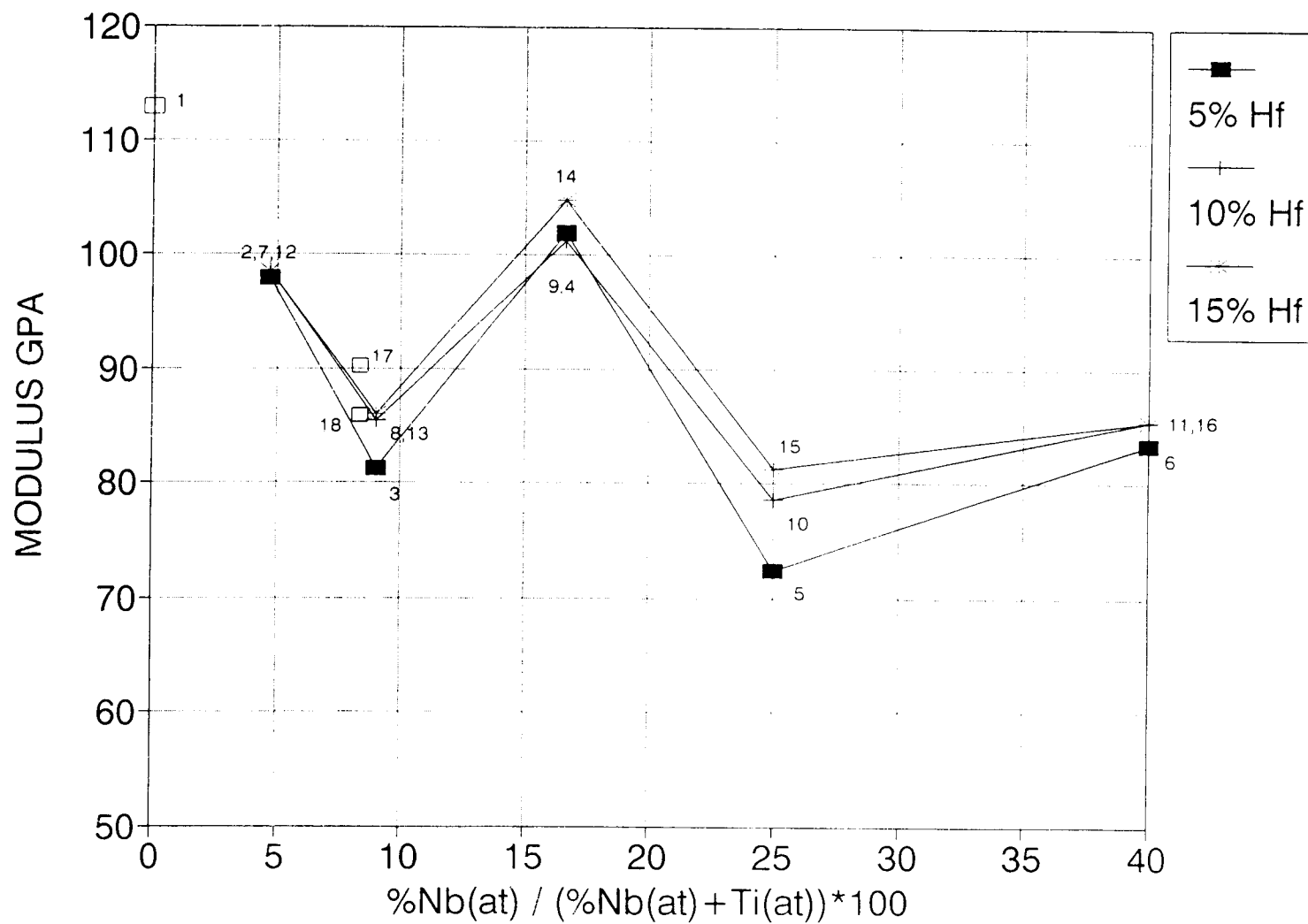


Figure 2 - Modulus Values vs. Composition (for as cast alloys)

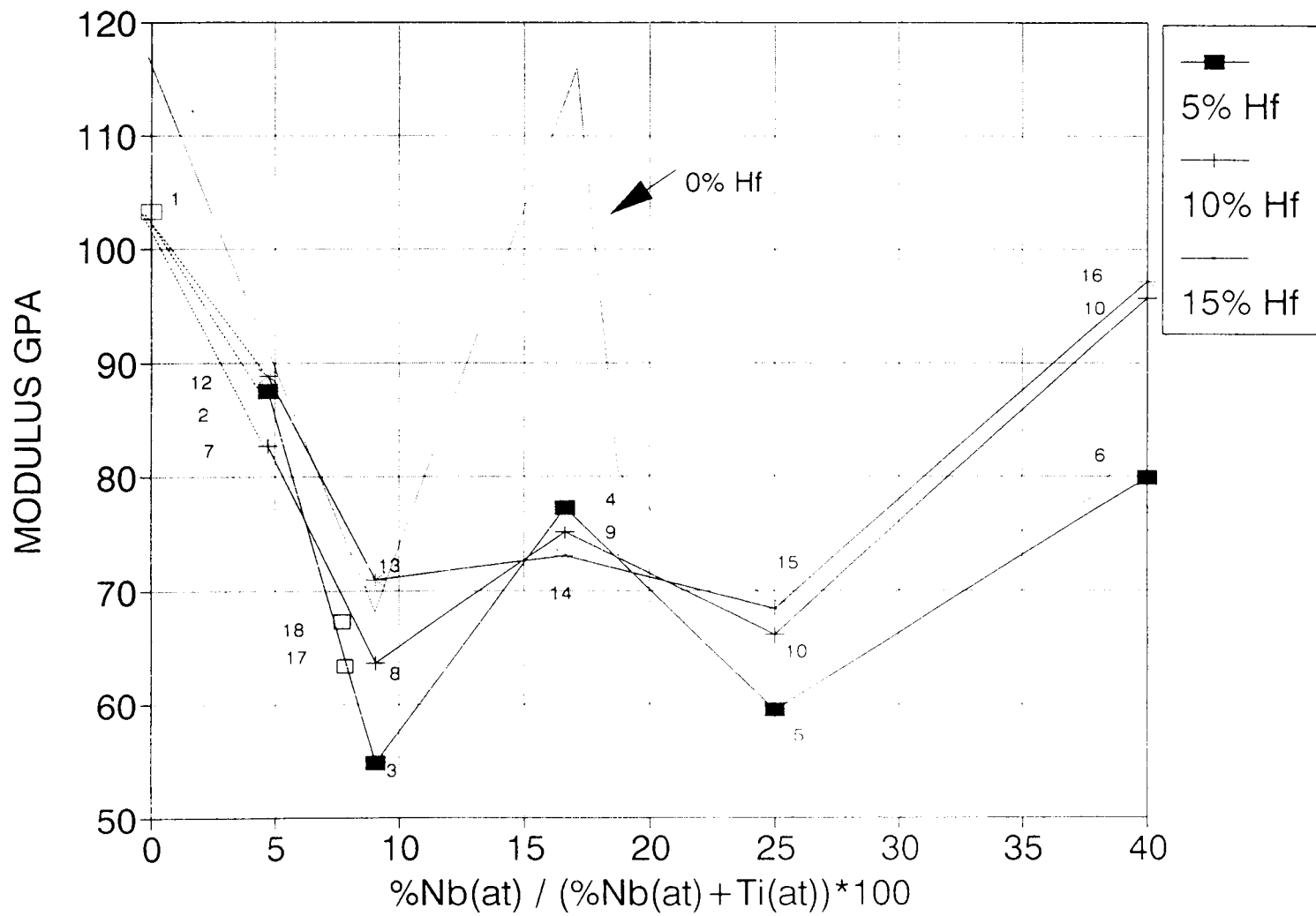


Figure 3- Modulus Values vs. Composition (for solution-treated & Quenched alloys)

TABLE 5. YOUNG'S MODULUS, AGED AT 500°C

Alloy	YOUNG'S MODULUS, AGED AT 500°C						
	As-quenched	Aged 1 hr	Aged 2 hr	Aged 3 hr	Aged 4 hr	Aged 5 hr	Aged 6 hr
1	103.4	107.5	106.8	106.8	107.5	106.8	106.8
2	87.5	91.0	91.0	91.6	91.0	91.6	91.6
3	54.7	66.8	68.6	69.6	70.3	71.0	71.7
4	77.2	84.8	87.5	88.9	91.6	91.6	91.6
5	59.5	65.0	65.5	68.6	68.3	67.2	68.2
6	79.9	84.1	84.1	84.1	84.1	84.1	84.1
7	82.7	95.1	95.8	95.8	95.8	95.8	96.5
8	63.7	84.1	85.4	86.8	87.5	88.2	88.9
9	75.1	95.1	103.4	101.3	109.6	91.0	98.5
10	66.1	73.7	75.8	80.6	79.9	76.5	77.2
11	95.8	92.3	92.3	92.3	92.3	92.3	91.6
12	88.9	100.6	101.3	101.3	101.3	101.3	101.3
13	71.0	91.0	93.0	95.1	96.5	97.8	98.5
14	73.0	110.3	111.6	108.9	110.3	111.6	107.5
15	68.3	89.6	110.3	88.2	80.6	88.9	79.2
16	97.2	95.1	95.1	94.4	95.1	94.4	94.4
17	64.2	77.9	80.6	80.6	81.3	82.0	82.7
18	67.3	74.4	75.1	75.1	75.8	75.8	75.8

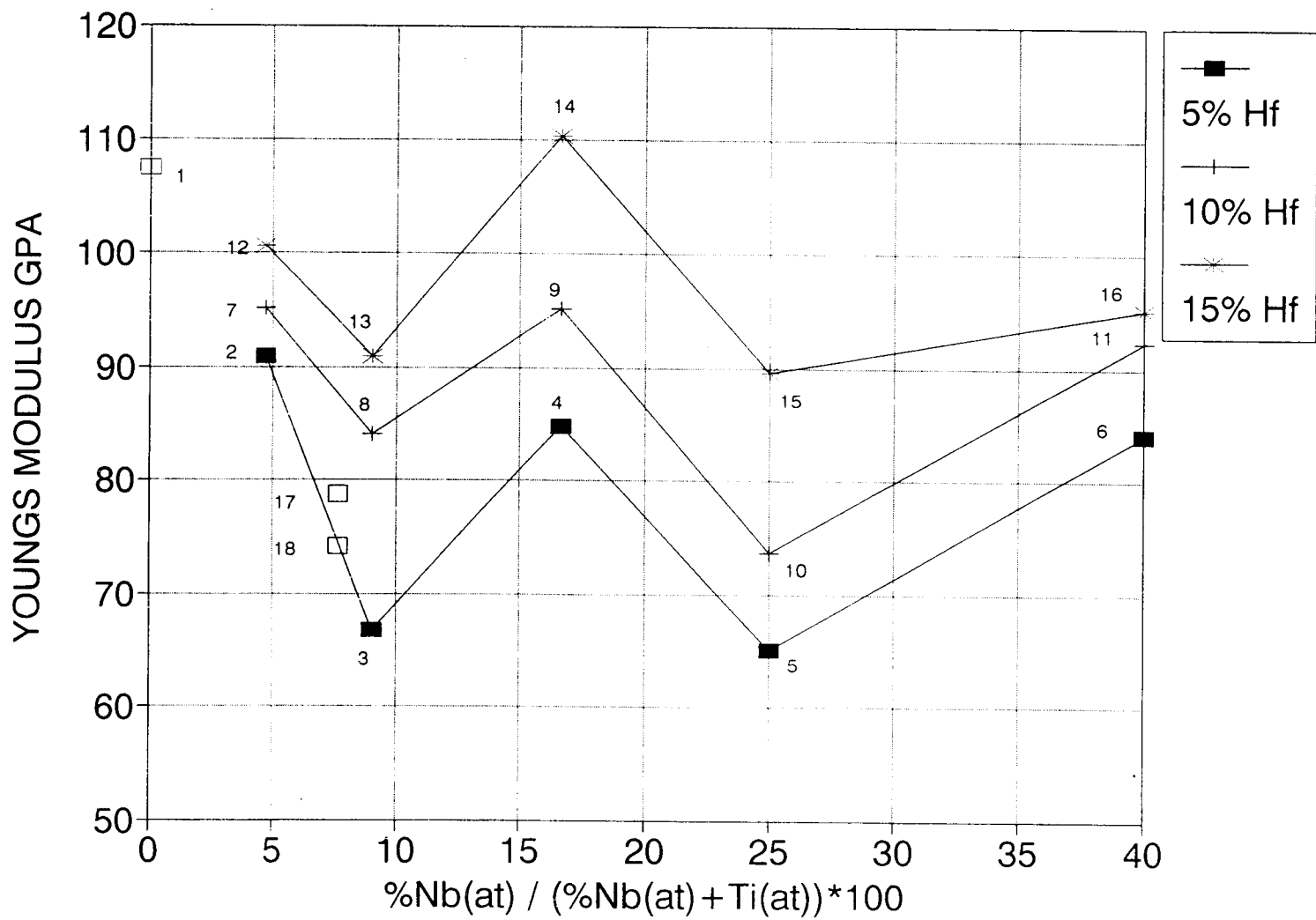


Figure 4 - Youngs Modulus vs. Composition (aged 1 Hr. @ 500 deg. C)

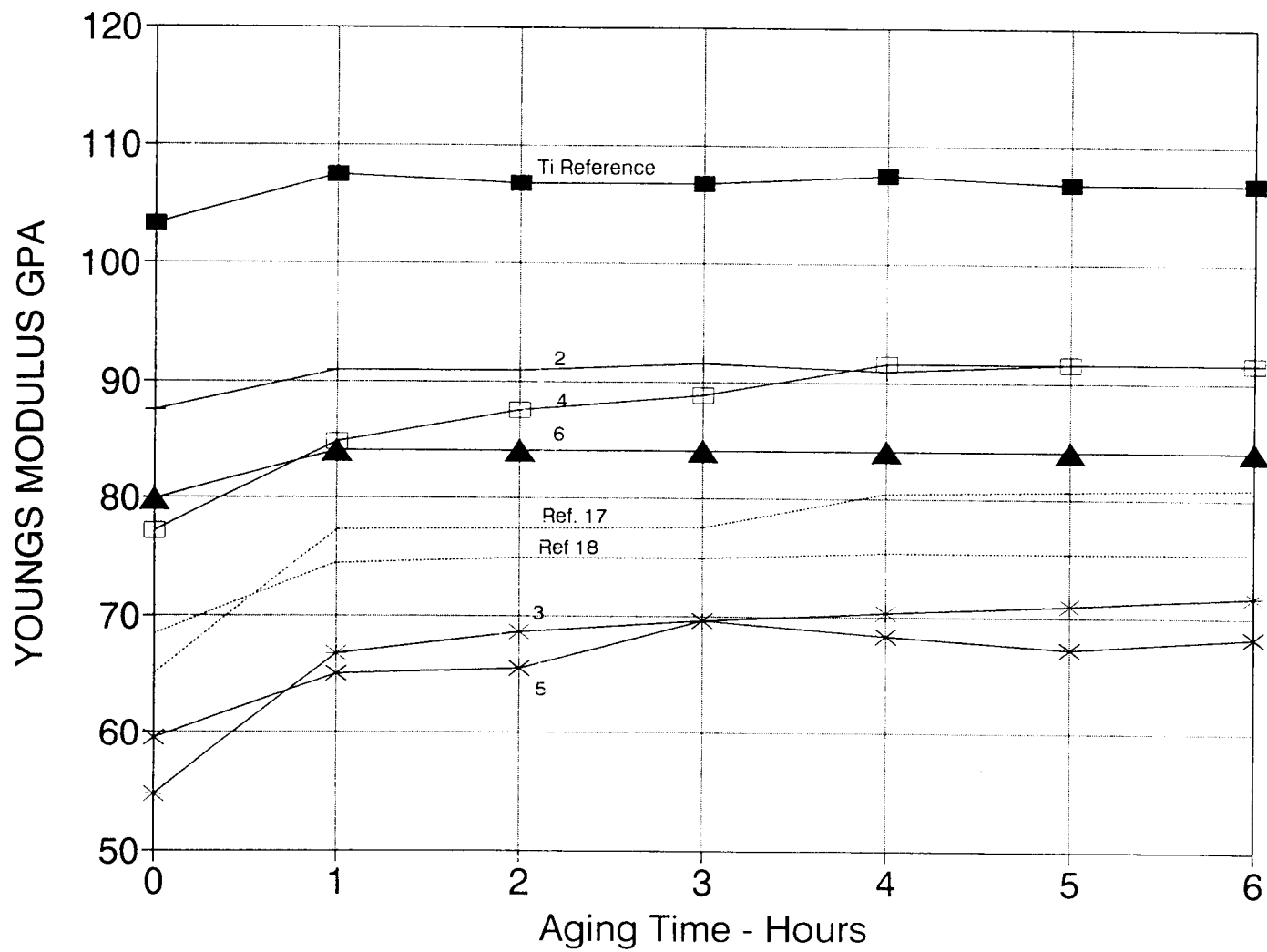


Figure 5 - Aging vs. Modulus - 5 at. % Hf Alloys

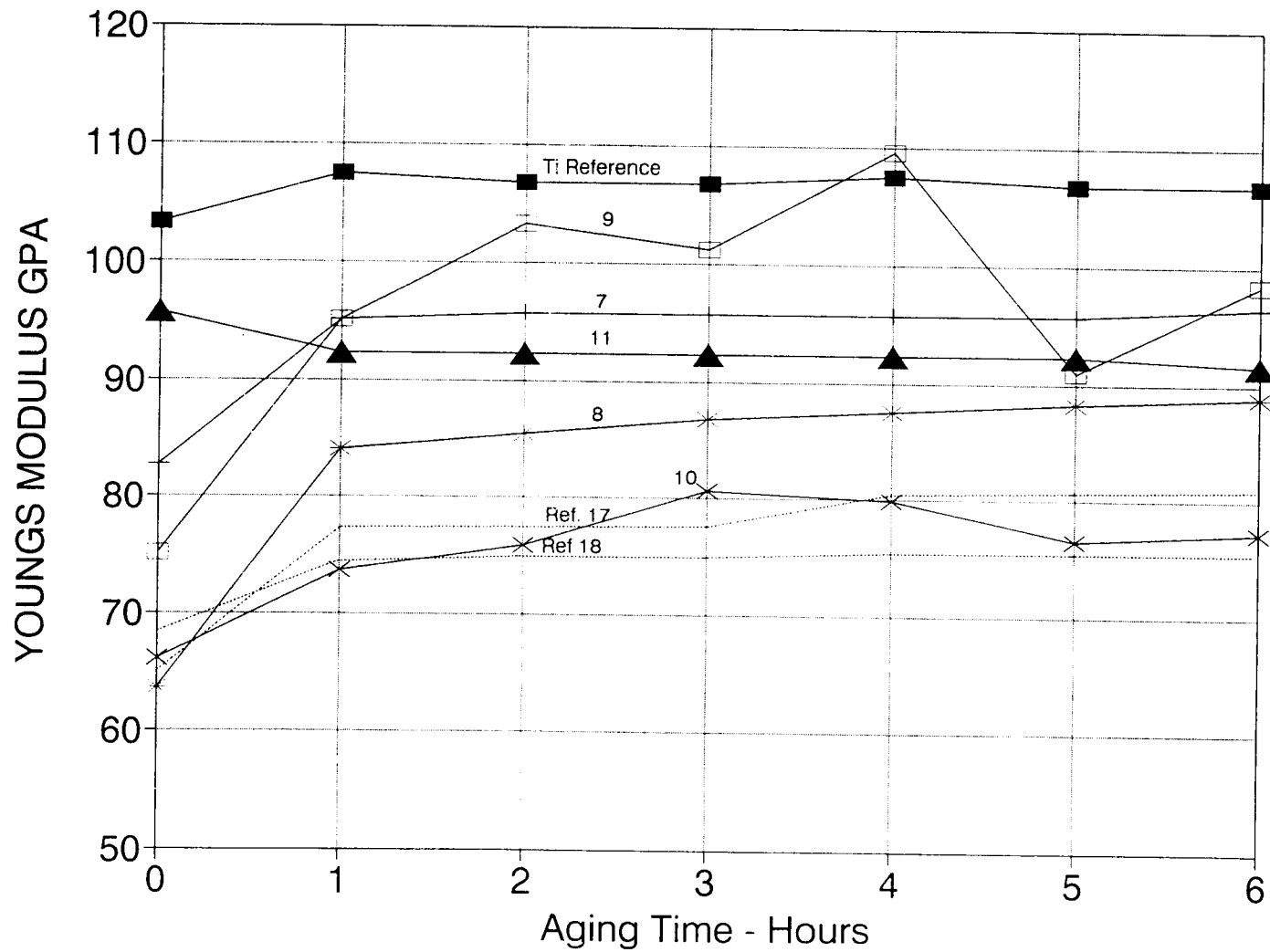


Figure 6 - Aging vs. Modulus - 10 at. % Hf Alloys

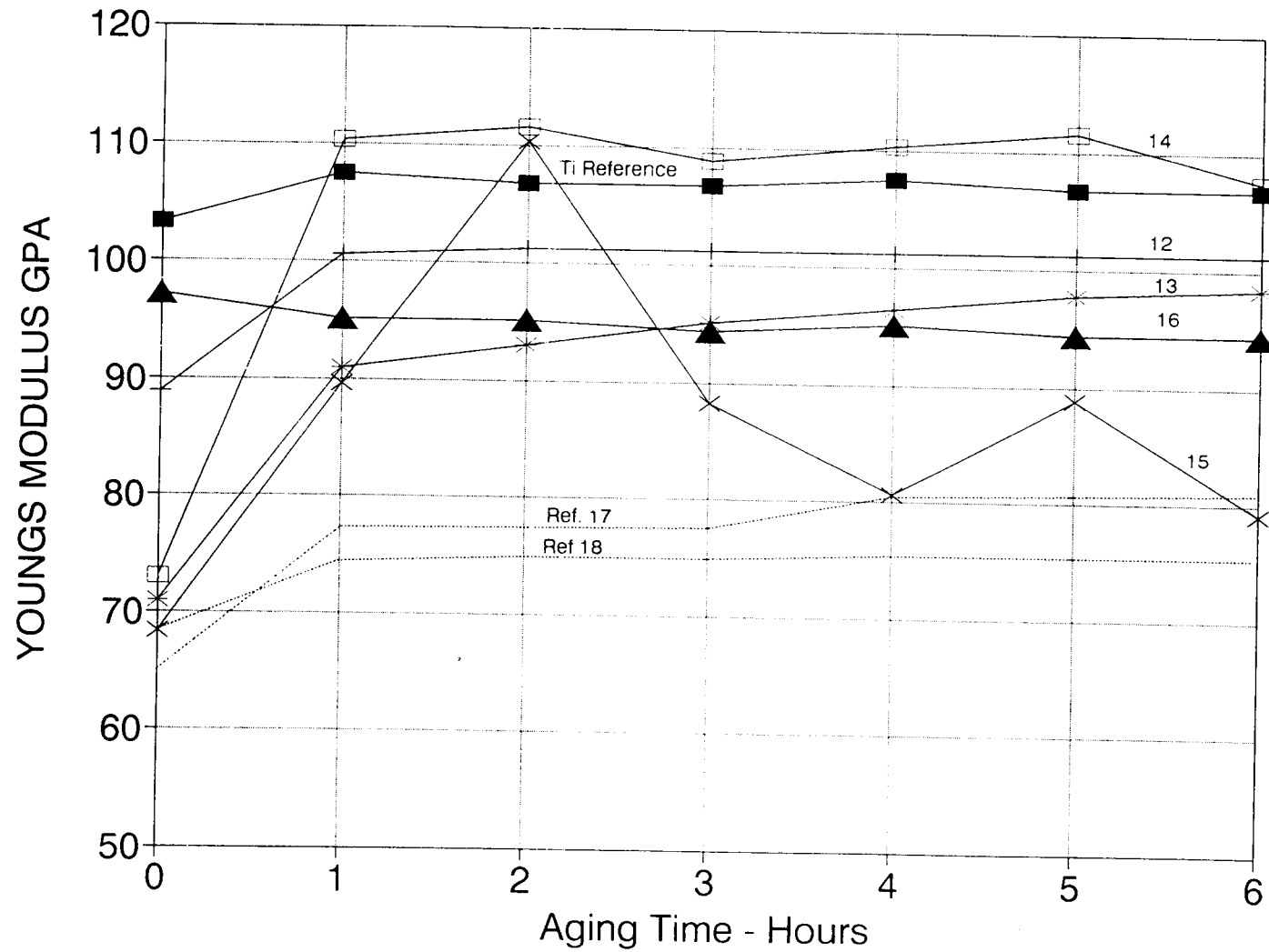


Figure 7 - Aging vs. Modulus - 15 at. % Hf Alloys

As shown, modulus values increase as these alloys are aged, with most compositions attaining a plateau in one to two hours.

Room temperature tensile testing results are recorded in Table 6 for the as-quenched and 6-hour-aged conditions. Data for yield strength (0.2% off-set) and ultimate strength as functions of composition and heat treatment are illustrated in Figures 8 and 9. Strength values increase significantly upon aging for alloys containing up to approximately 35 atomic % Nb ($\text{Nb}/(\text{Nb}+\text{Ti})$).

Table 7 presents a comparison of Young's modulus values obtained for as-quenched and six-hour-aged specimens by the two different methods employed: IRA and tensile testing. The variability indicated in Table 7 resulted in two precautionary actions to be implemented in subsequent experiments:

- 1) A "pinned" type of tensile testing specimen would be used to ensure that no slippage would occur during the test.
- 2) In an effort to improve chemical homogeneity, pre-alloyed Nb (e.g., NbTi), rather than pure Nb, would be utilized for subsequent alloy melting. (As noted previously, the presence of small, high-density inclusions in some specimens was revealed by X-radiography.)

TABLE 6. TENSILE PROPERTIES

Alloy	AS-QUENCHED				AGED 6 HR. @ 500°C			
	YS, MPa	UTS, MPa	% El.	Mod., GPa	YS, MPa	UTS, MPa	% El.	Mod., GPa
1	235.7	386.6	37	89.6	237.1	385.2	34	107.5
2	534.8	709.1	13	84.1	592.0	700.8	13	103.4
3	359.7	626.4	24	48.9	757.4	857.3	8	75.1
4	279.1	528.6	27	58.6	668.5	768.4	9	91.0
5	350.1	516.2	31	56.5	717.4	751.8	5	74.4
6	445.9	494.1	19	71.0	503.8	534.1	18	89.6
7	535.5	820.1	15	81.3	747.7	897.9	6	89.6
8	378.3	709.1	13	60.0	922.1	925.5	0	83.4
9	306.7	590.6	21	60.6	698.1	831.1	5	94.4
10	430.7	536.2	27	57.9	762.2	762.2	2	88.2
11	666.4	748.4	12	75.1	735.3	791.1	15	88.2
12	660.9	910.4	11	66.8	839.4	1017.8	3	88.2
13	441.7	741.5	16	54.4	986.8	1085.4	2	87.5
14	384.5	683.6	12	73.7	--	741.5	--	--
15	420.4	582.3	22	67.5	849.0	959.3	0	86.1
16	592.0	625.7	16	74.4	622.3	655.4	9	84.8
17	394.9	691.2	17	76.5	811.1	828.3	1	79.2
18	452.1	681.6	15	68.2	677.4	787.0	4	64.8

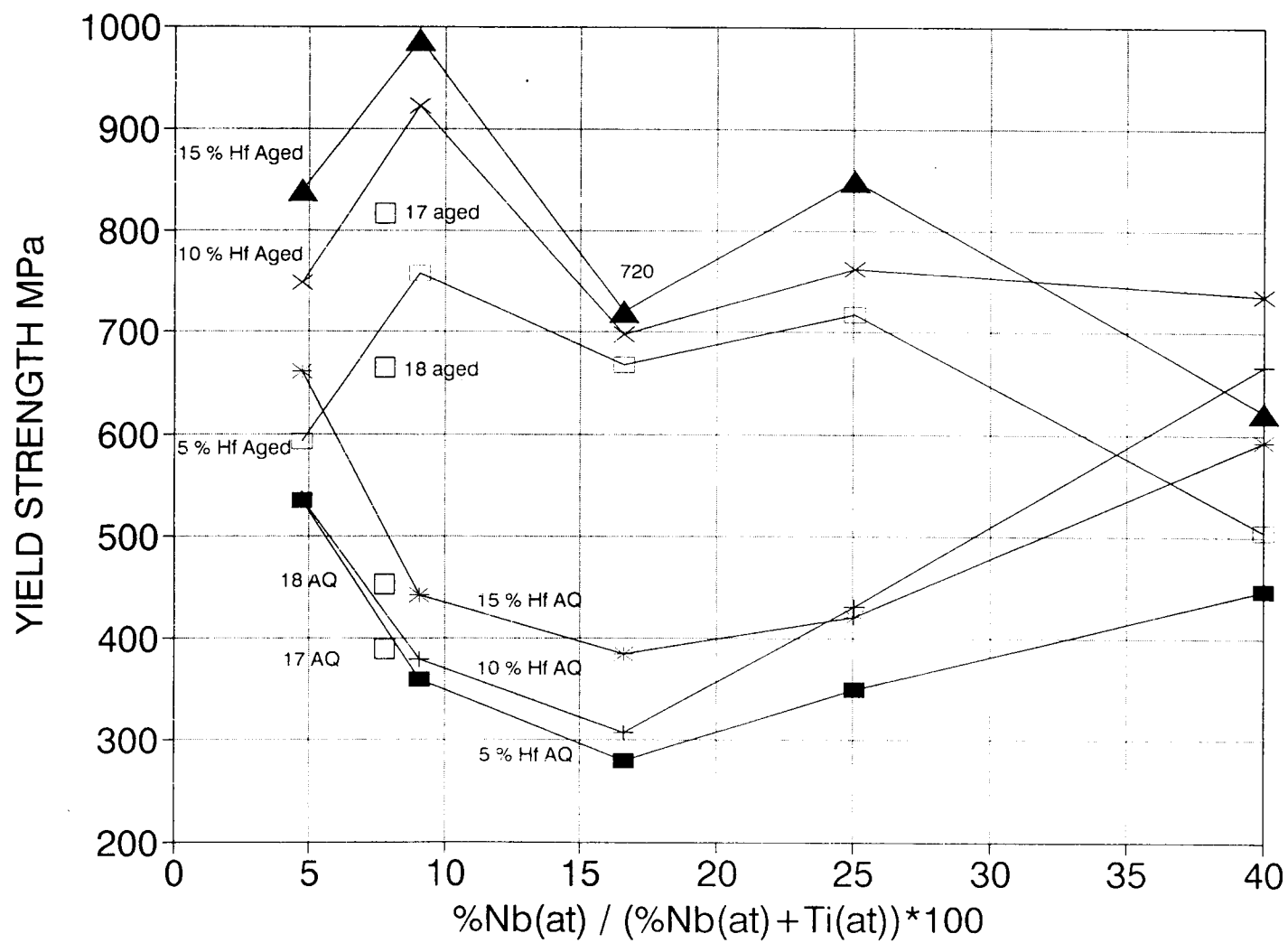


Figure 8 - Effect of Aging on Yield Strength (6 Hr. @ 500 deg. C)

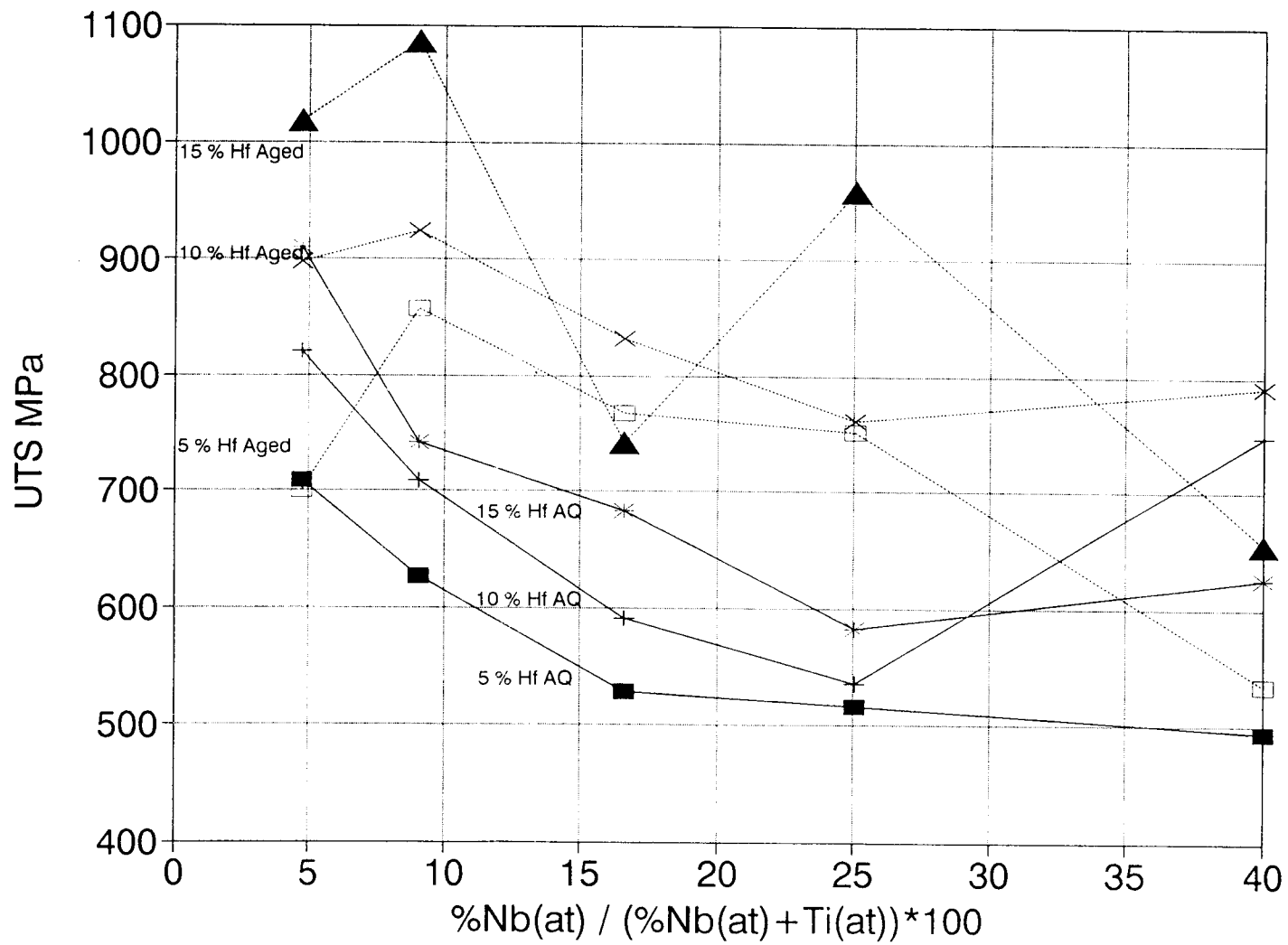


Figure 9 - Effect of Aging on UTS (6Hr. @ 500 deg. C)

TABLE 7. COMPARISON OF MODULUS MEASUREMENT METHODS

Alloy	As-quenched Modulus, GPa		6-hr Aged Modulus, GPa	
	IRA	Tensile	IRA	Tensile
1	103.4	89.6	106.8	107.5
2	87.5	84.1	91.6	103.4
3	54.7	48.9	72.4	75.1
4	77.2	58.6	91.6	91.0
5	59.5	56.5	80.6	74.4
6	79.9	71.0	84.8	89.6
7	82.7	81.3	96.5	89.6
8	63.7	60.0	89.6	83.4
9	75.1	60.6	104.7	94.4
10	66.1	57.9	90.3	88.2
11	95.8	75.1	93.0	88.2
12	88.9	66.8	102.0	88.2
13	71.0	54.4	101.3	87.5
14	73.0	73.7	122.7	--
15	68.3	67.5	104.1	86.1
16	97.2	74.4	95.8	84.8
17	64.2	76.5	82.7	79.2
18	67.3	68.2	76.5	64.8

Due to the fact that all specimens had been rapidly cooled in water from the 500°C aging temperature for expediency, it was decided to investigate possible effects of slower cooling on modulus values. The specimens which had been aged for six hours at 500°C were therefore reheated to 500°C for ten minutes, followed by air cooling. As indicated in Table 8, some modulus values increased as a result of air cooling. For this reason, all subsequent aging studies utilized air cooling.

TABLE 8. EFFECT OF COOLING RATE FROM 500°C ON MODULUS (IRA METHOD)

Alloy	YOUNG'S MODULUS, GPa		
	Water-cooled	Air-cooled	Change
1	106.8	106.8	0
2	91.6	91.6	0
3	71.7	72.4	+ 0.7
4	91.6	91.6	0
5	68.2	80.6	+12.4
6	84.1	84.8	+ 0.7
7	96.5	96.5	0
8	88.9	89.6	+ 0.7
9	98.5	104.7	+ 6.2
10	77.2	90.3	+13.1
11	91.6	93.0	+ 1.4
12	101.3	102.0	+ 0.7
13	98.5	101.3	+ 2.8
14	107.5	122.7	+15.2
15	79.2	104.1	+24.9
16	94.4	95.8	+ 1.4
17	82.7	82.7	0
18	75.8	76.5	+ 0.7

B. Phase II

Table 9 presents density as a function of composition for the 16 experimental alloys of Phase III.

Young's modulus values are presented in Table 10 for as-quenched specimens and for specimens aged at 500°C for times of 0.5, 1.5, 2.5, 4.0, and 6.0 hours.

Figure 10 illustrates the effect of Hf concentration on Young's modulus for the 10 and 40 atomic % Nb alloys. (The value shown for Alloy 24 (10%Nb 5%Hf) appears to be spurious in relation to other values.) The lower modulus value obtained for the binary TiNb alloy, in comparison with earlier published values, may be due to lower impurity levels in modern material or to some difference in heat treating parameters.

Figure 11 shows an example (Alloy 28) of the effect of aging time at 500°C on Young's modulus. Other 10% Nb compositions have similar curves according to the data of Table 10.

As a means of establishing variability in IRA Young's modulus values, specimens representing the fully aged (6 hours @ 500°C) condition were sheared in half lengthwise, followed by modulus measurement of each half,

TABLE 9. COMPOSITION VS. DENSITY

Alloy	Atomic %			Weight %			Atomic Ratio	Density
	Ti	Nb	Hf	Ti	Nb	Hf	Nb/ (Nb+Ti)	g/cm ³
19	60.	40.	0	43.6	56.4	0	40	6.105
20	90.	10.	0	82.3	17.7	0	10	4.850
21	56.4	37.6	6	37.18	48.08	14.74	40	6.549
22	84.6	9.4	6	67.58	14.56	17.86	10	5.514
23	57	38.	5	38.17	49.35	12.48	40	6.580
24	85.5	9.5	5	69.76	15.03	15.21	10	5.464
25	57.6	38.4	4	39.19	50.67	10.14	40	6.436
26	86.4	9.6	4	72.05	15.53	12.43	10	5.313
27	58.2	38.8	3	40.43	52.27	7.77	40	6.396
28	87.3	9.7	3	74.43	16.04	9.53	10	5.183
29	58.8	39.2	2	41.33	53.43	5.24	40	6.242
30	88.2	9.8	2	76.92	16.58	6.50	10	5.013
31	59.4	39.6	1	42.45	54.89	2.66	40	6.239
32	89.1	9.9	1	79.53	17.14	3.33	10	4.996
33	84.55	7.75	7.8	65.72	11.68	22.59	8.4	5.660
34	84.55	7.75	7.8 Zr, no Hf	73.88	13.13	12.98 Zr, no Hf	8.4	5.002

TABLE 10. YOUNG'S MODULUS VALUES (GPa)
(IRA METHOD)

Alloy	As-quenched	Aged at 500°C				
		0.5 hr	1.5 hr	2.5 hr	4.0 hr	6.0 hr
19	82.7	83.4	83.4	82.7	82.7	82.7
20	54.6	64.6	66.2	69.6	77.9	72.4
21	86.1	84.8	84.8	84.1	84.1	83.4
22	54.2	71.0	77.9	75.8	77.2	76.5
23	89.6	91.0	89.6	89.6	89.6	87.5
24	70.3	79.2	78.6	80.6	81.3	80.6
25	86.8	87.5	87.5	86.1	85.4	85.4
26	55.0	72.4	78.6	77.2	79.2	81.3
27	86.1	87.5	87.5	87.5	86.8	84.8
28	54.3	70.3	74.4	72.2	75.1	75.8
29	84.8	85.4	86.8	84.8	84.1	84.8
30	55.1	71.0	72.4	73.7	75.8	77.2
31	84.8	91.0	86.1	84.1	84.1	82.0
32	62.6	72.4	73.0	72.2	74.4	73.7
33	61.2	71.7	73.7	72.4	72.2	72.4
34	66.4	75.8	81.3	76.5	78.6	79.2

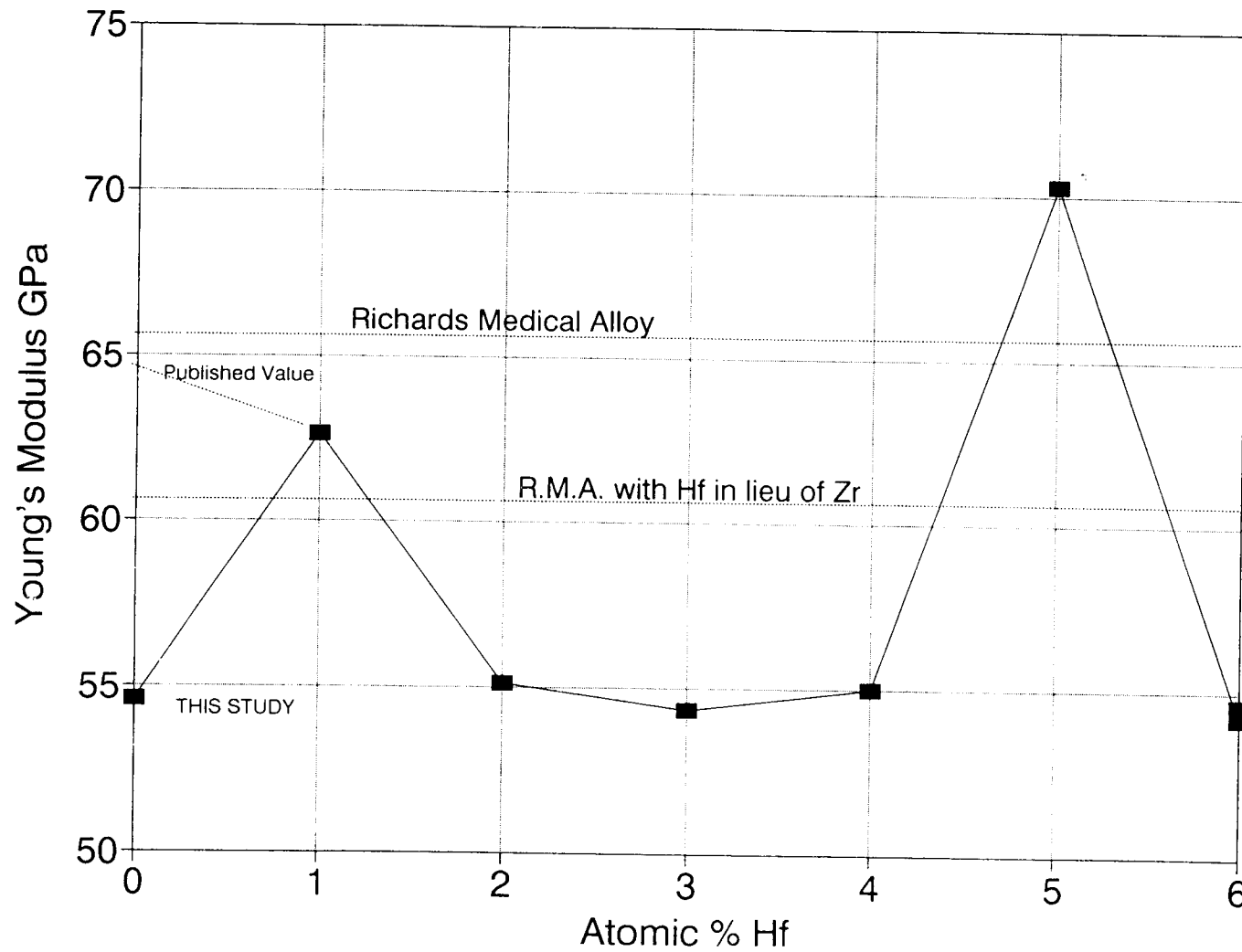


Figure 10 - Effect on Modulus of Hf Additions to Nb/(Nb+Ti) = 10 at. % Alloy (As Quenched from 850 C)

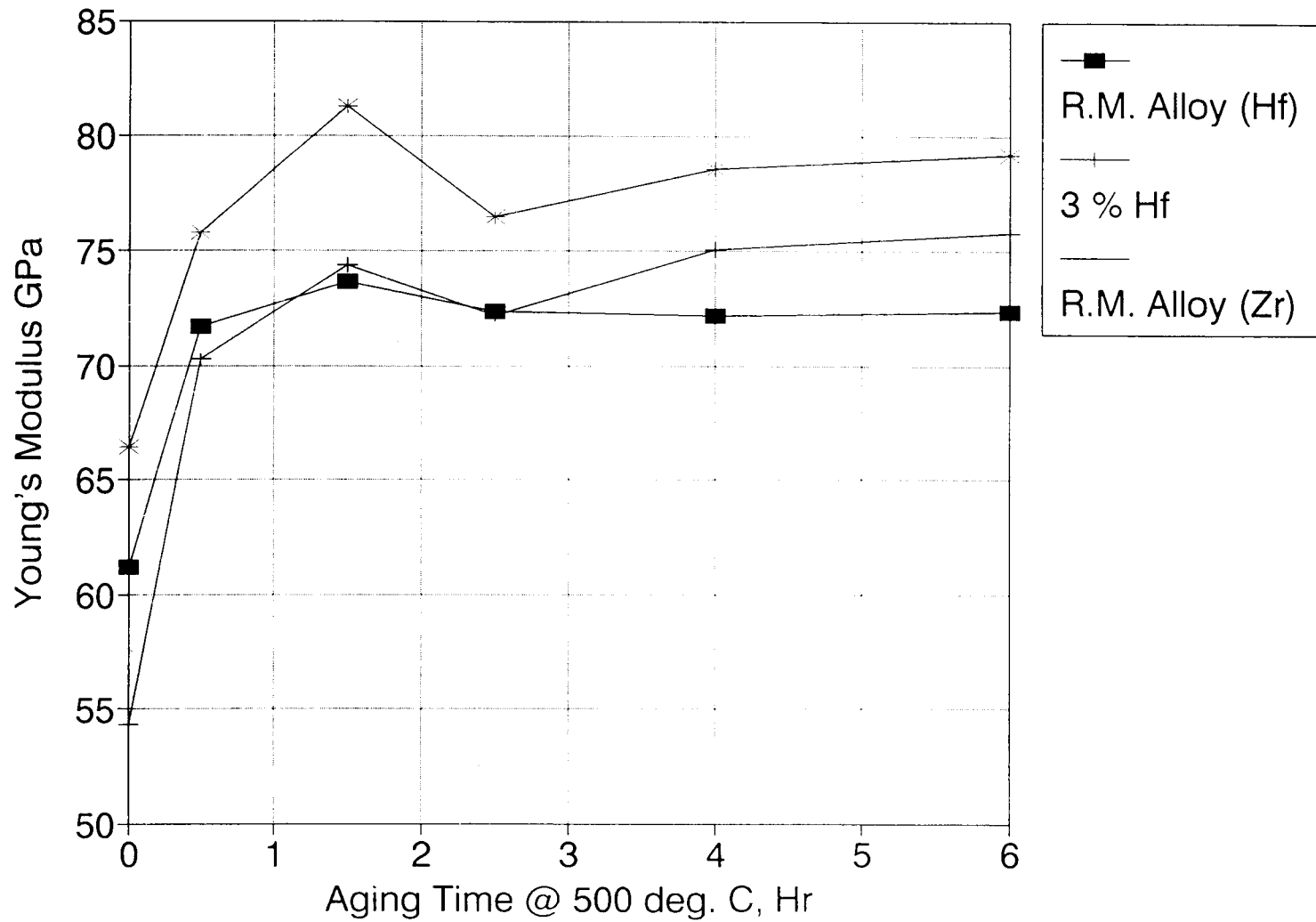


Figure 11 - Aging vs. Modulus

as presented in Table 11. The "B" specimens of Table 11 were reheated to 850°C, soaked for 1.0 hour, quenched in water, and remeasured for Young's modulus.

Values obtained are presented in Table 12, along with the original as-quenched values for comparison. The requenched values are generally higher than original values, perhaps suggesting that the soaking time at 850°C was inadequate.

The "A" (aged) and "B" (re-quenched) specimens were tensile tested at room temperature. Yield strength, ultimate tensile strength, percent elongation, and Young's modulus are presented in Table 13. Figures 12 and 13 illustrate the effect of aging for six hours at 500°C on yield strength and ultimate tensile strength for alloys containing 10 and 40 atomic % Nb, respectively. A significant age-hardening effect is apparent for alloys with 10 atomic % Nb.

The precaution of utilizing pinned specimens to prevent any possibility of slippage during tensile testing resulted in values for Young's modulus which were directly compared against corresponding ultrasonically determined values. Table 14 presents data comparisons of these two methods. Vickers hardness values are presented

TABLE 11. VARIABILITY IN MODULUS MEASUREMENT
(IRA METHOD)

Alloy	YOUNG'S MODULUS, GPa		
	Sample A	Sample B	Difference (A-B)
19	81.3	83.1	- 1.8
20	75.8	73.7	+ 2.1
21	80.6	83.4	- 2.8
22	81.3	77.2	+ 4.1
23	83.1	87.5	- 4.4
24	75.1	78.6	- 3.5
25	82.0	84.8	- 2.8
26	84.8	80.6	+ 4.2
27	83.1	85.4	- 2.3
28	79.2	76.5	+ 2.7
29	82.0	85.4	- 3.4
30	79.2	77.2	+ 2.0
31	81.3	83.1	- 1.8
32	72.3	75.8	- 3.5
33	75.8	72.3	- 3.5
34	80.6	77.2	- 3.4

TABLE 12. EFFECT OF REQUENCHING AGED SPECIMENS

Alloy	YOUNG'S MODULUS, GPa (IRA)		
	Original	Requenched	Difference (O-R)
19	82.7	86.1	- 3.4
20	54.6	60.8	- 6.2
21	86.1	88.2	- 2.1
22	54.8	61.7	- 6.9
23	89.6	90.3	- 0.7
24	70.3	69.6	+ 0.7
25	86.8	88.2	- 1.4
26	55.0	61.9	- 6.9
27	86.1	87.5	- 1.4
28	54.3	59.7	- 5.4
29	84.8	87.5	- 2.7
30	55.1	60.6	- 5.5
31	84.8	85.4	- 0.6
32	62.6	62.3	+ 0.3
33	61.2	63.8	- 2.6
34	66.4	66.3	+ 0.1

TABLE 13. TENSILE PROPERTIES*

Alloy	AS QUENCHED				AGED 6 HR @ 500°C			
	YS, MPa	UTS, MPa	% EL.	MOD., GPa	YS,MPa	UTS, MPa	% EL	MOD., GPa
19	401.1	392.1	7	83.8	436.6	452.4	6	89.4
20	296.7	548.6	11.5	58.6	637.4	829.4	6.5	82.9
21	474.5	499.6	6	84.4	537.5	556.1	5	92.9
22	462.1	640.6	9	63.9	894.8	953.4	2.5	86.3
23	588.2	615.4	5.5	84.4	626.8	651.9	6	91.5
24	396.2	618.8	13	67.3	694.0	771.5	5	80.2
25	462.1	483.4	7	84.2	508.9	531.0	5	93.4
26	295.0	585.4	12.5	69.9	880.7	943.8	1.5	87.8
27	444.8	468.6	9.5	79.6	486.2	502.7	7	83.0
28	270.8	585.8	15.5	71.1	808.0	892.1	3	79.6
29	423.1	441.4	9	87.9	457.2	477.2	9	85.9
30	277.7	566.5	15.5	61.2	782.9	888.0	2.5	86.4
31	424.2	445.9	9	81.6	449.3	465.8	7	84.1
32	270.1	551.7	15.5	56.7	661.6	767.7	4	72.8
33	472.8	736.0	13	65.6	745.0	853.2	5.5	76.4
34	411.4	670.9	11	63.5	741.9	855.2	4.5	79.2

* Each data point represents the average of two values.
All specimens were tested parallel to the rolling direction.

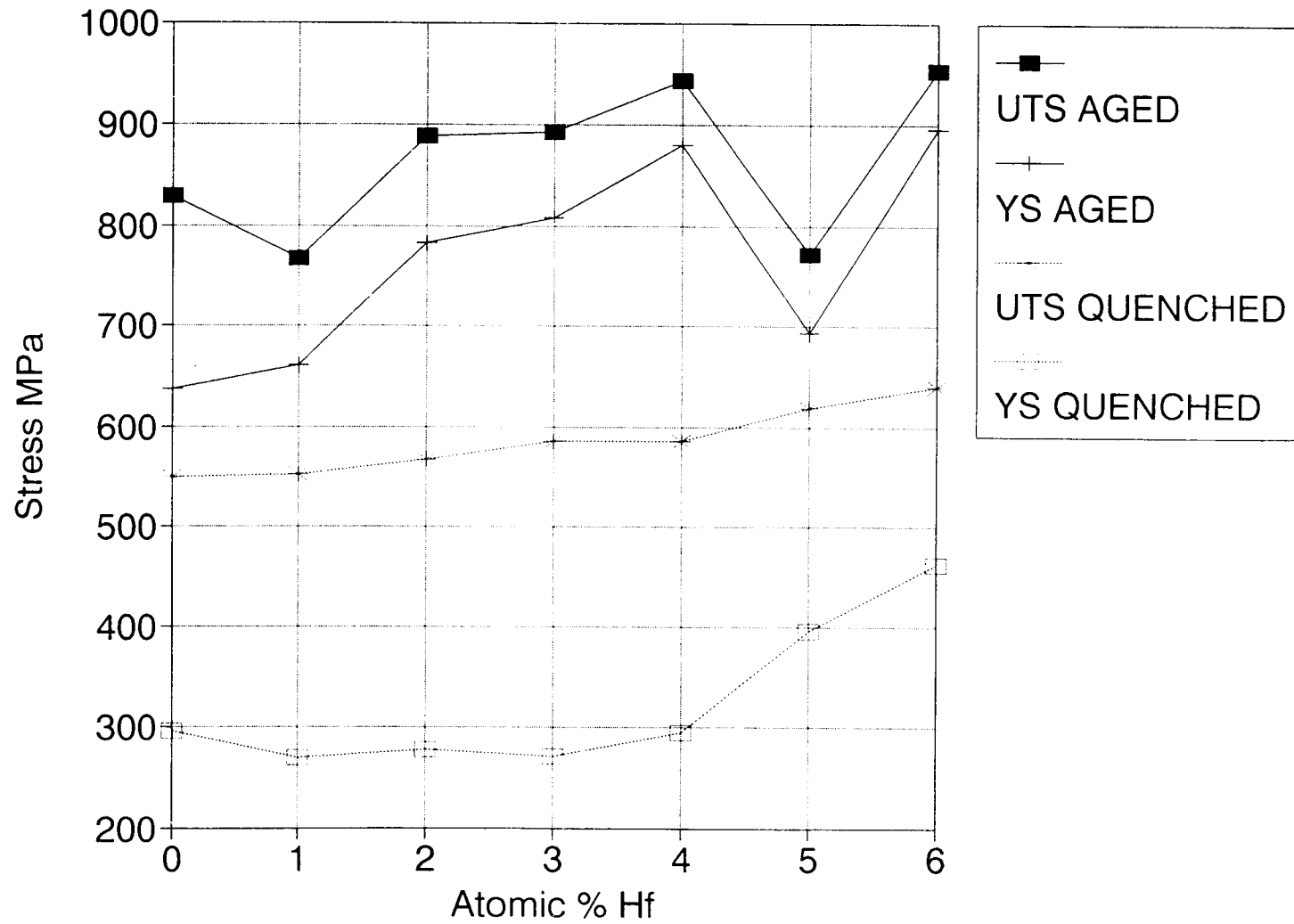


Figure 12 - YS / UTS vs. At.% Hf 10 at. % Nb Alloys

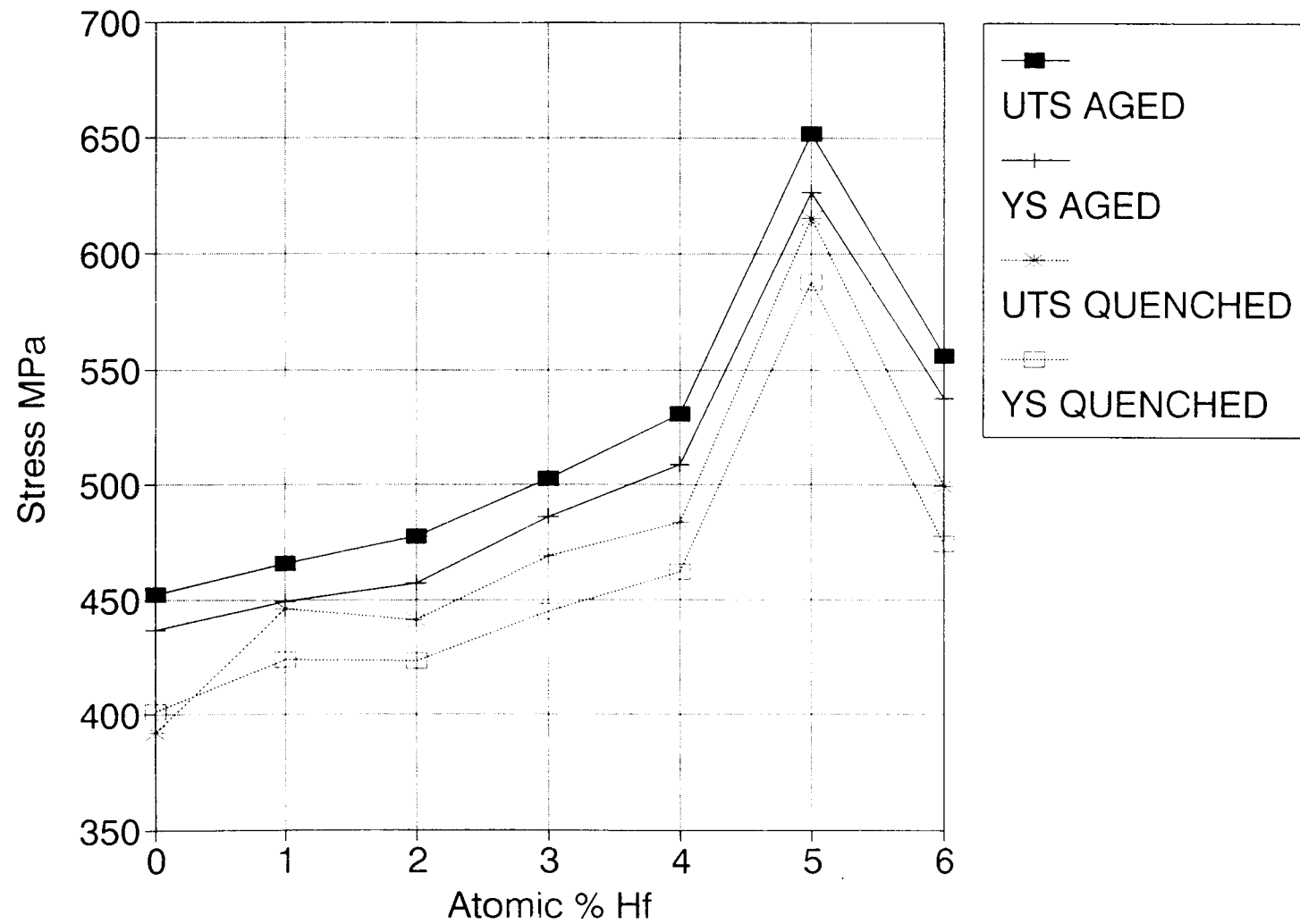


Figure 13 - YS / UTS vs. At. % Hf 40 at. % Nb Alloys

TABLE 14. COMPARISON OF MODULUS MEASUREMENTS METHODS

Alloy	** AS-QUENCHED MODULUS, GPa			* 6-HR. AGED MODULUS, GPa		
	IRA	Tensile	$\Delta_{(U-T)}$	IRA	Tensile	$\Delta_{(U-T)}$
19	86.1	83.8	+ 2.3	81.3	89.4	- 8.1
20	60.8	58.6	+ 2.2	75.8	82.9	- 7.1
21	88.2	84.4	+ 3.8	80.6	92.9	-12.3
22	61.7	63.9	- 2.2	81.3	86.3	- 5.0
23	90.3	84.4	+ 5.9	83.1	91.5	- 8.4
24	69.6	67.3	+ 2.3	75.1	80.2	- 5.1
25	88.2	84.2	+ 4.0	82.0	93.4	-11.4
26	61.9	63.9	- 2.0	84.8	87.8	- 3.0
27	87.5	79.6	+ 7.9	83.1	83.0	+ 0.1
28	59.7	71.1 (?)	-11.4 (?)	79.2	79.6	- 0.4
29	87.5	87.9	- 0.4	82.0	85.9	- 3.9
30	60.6	61.2	- 0.6	79.2	86.4	- 7.2
31	85.4	81.6	+ 3.8	81.3	84.1	- 2.8
32	62.3	56.7	+ 5.6	72.3	72.8	- 0.5
33	63.8	65.6	- 1.8	75.8	76.4	- 0.6
34	66.3	63.5	+ 2.8	80.6	79.2	+ 1.4

* "A" specimens

** "B" specimens

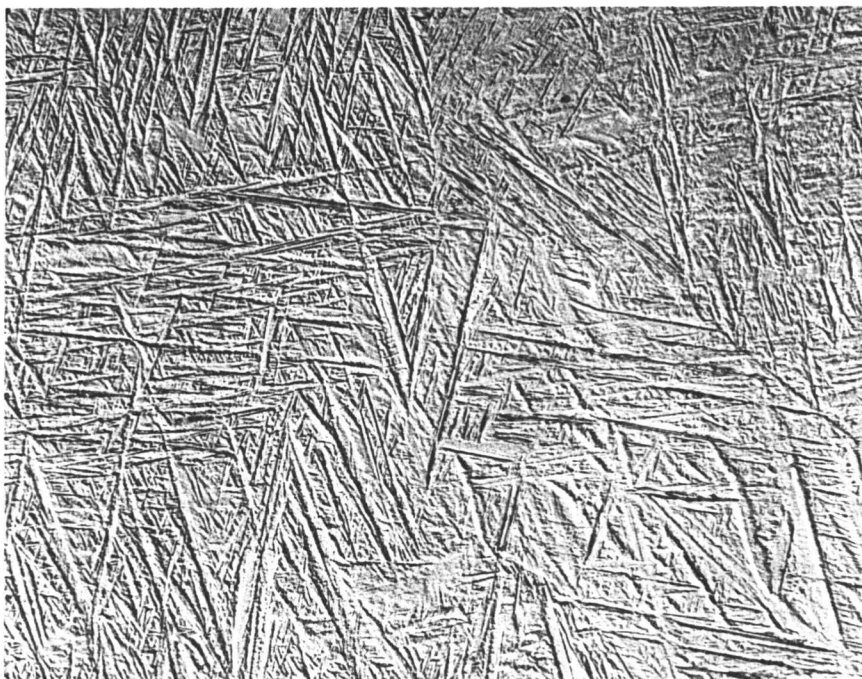
in Table 15 which also illustrates the significant effect of aging in the 10 atomic % Nb alloys.

TABLE 15. VICKERS HARDNESS (H_V)

Alloy	HARDNESS (H_V)	
	As-Quenched	Aged 500°C, 6 hrs
19	139	148
20	169	212
21	162	175
22	202	269
23	194	204
24	200	319
25	157	166
26	185	315
27	157	170
28	180	318
29	149	161
30	177	294
31	146	159
32	170	204
33	215	260
34	207	264

Examples of typical microstructures for the 10- and 40-atomic % Nb alloys are presented in Figures 14 and 15, respectively. The expected martensitic structure of quenched 10 at. % Nb alloys is evident and unaffected by variations in Hf content between 0 and 6 at. %. After aging, the structure has a typical "tempered martensite" morphology. (As mentioned previously, the alpha precipitates are apparently submicroscopic in size.) As would also be expected from the TiNb binary-phase diagram, alloys containing 40 at. % Nb display a single-phase (beta) structure. Aging at 500°C did not visibly change the morphology of the as-quenched structure, as this temperature lies above the beta transus.

Although the exact mechanism accounting for the two modulus minima (illustrated in Figure 3 of Phase I Results) is not understood, these studies confirm their correlation with electron/atom ratios of about 4.10 and 4.22 (Table 1).

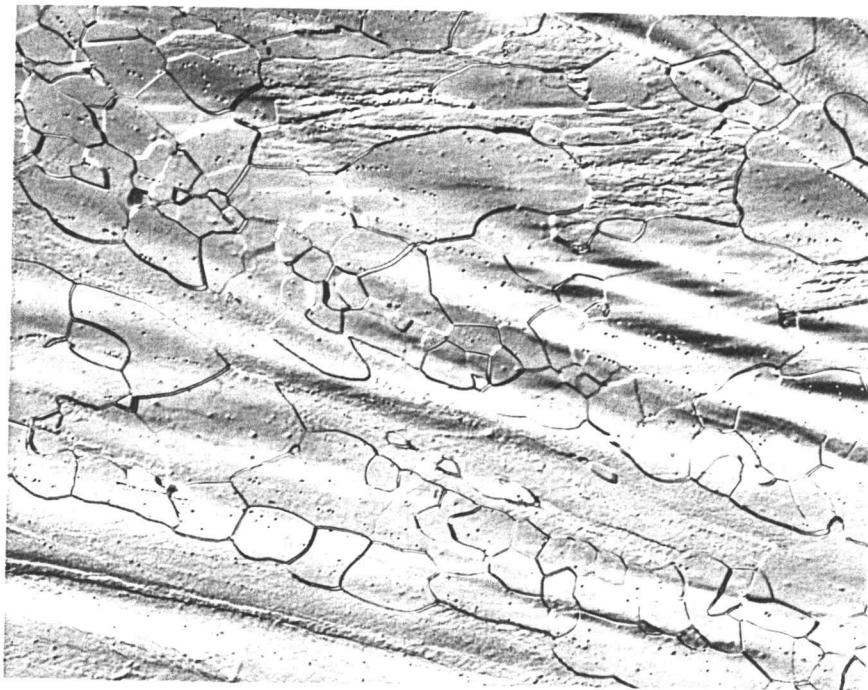


As-Quenched (Alloy 28) 200X



Aged 6 hr. @ 500°C (Alloy 28) 200 X

Figure 14. Microstructure of Alloys with 10 at. % Nb



As-Quenched (Alloy 27) 200X

Figure 15. Microstructure of Alloys with 40 at. % Nb

V. CONCLUSIONS

While much work remains to be done by which such properties as wear resistance, corrosion resistance, fatigue resistance, and biocompatibility may be determined, the following preliminary observations provide encouragement to eventually propose certain TiNbHf alloys for orthopedic applications.

- 1) Alloys with approximately 10 atomic % Nb (~16 wt. %) may be quenched from 850°C to obtain low Young's modulus (~ 60 GPa). The modulus is unaffected by 0-6 atomic % Hf concentrations.
- 2) Alloys with approximately 40 atomic % Nb (~50 wt. %) display considerably higher Young's modulus values (~ 85 GPa) in the as-quenched condition. Hf concentration again seems to have little effect on modulus.
- 3) Very significant strengthening occurs upon aging the quenched 10 at. % Nb alloys at 500°C. Hf additions further contribute significantly to this strengthening. Yield strengths of several such alloys more than tripled during aging (from 275 MPa/40 ksi to 895 MPa/130 ksi). Even the binary NbTi alloy increased in yield strength from 275 MPa/40 ksi to 634 MPa/92 ksi. By comparison with these values, the proposed

commercial Ti13Zr13Nb (wt. %) alloy attained an aged yield strength of 742 MPa/107 ksi.

- 4) The heat treating processes used in this study probably do not represent optimum parameters. Requenched modulus data indicate that longer solution heat treating times should be utilized, which could possibly further improve the aged strength values. Furthermore, there is no reason to believe that 500°C represents the optimum aging temperature for these alloys.
- 5) The "impulse response" modulus measurement method is a convenient and useful tool in studies such as this one. Measurements coincide quite well (± 3.4 GPa/0.5 Mpsi) with tensile testing results.

The apparently superior strengthening effect of Hf, as compared to Zr, additions to Ti alloys with approximately 10 atomic % Nb provides an incentive to pursue biocompatibility studies with the ultimate goal of obtaining FDA and other necessary approvals.

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