

FACTORS INFLUENCING THE STABILITY OF NICKEL-BASE  
HIGH-TEMPERATURE ALLOYS

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Abstract

The stability of nickel-base high-temperature alloys at elevated temperature is discussed in relation to structural changes which can occur under certain conditions liable to occur in service. Particular attention is given to associated effects on mechanical properties.

The influence of composition and heat treatment, on formation and growth of phases in iron-rich nickel alloys and iron-free high-strength wrought and cast nickel-base alloys are reviewed, on the basis of research carried out to develop improved alloys of the respective types. Attention is drawn to precautions which may be taken in selection and control of composition and heat treatment, to achieve maximum stability of properties. It is urged that the nature of individual types of structural instability, and their respective effects on properties, should be adequately evaluated before restricting the use of alloys for specific applications.

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## Introduction

With the advent of stronger and more highly alloyed materials, to meet the requirements of design engineers in achieving improved performance at higher operating temperatures, the significance of structural stability in nickel-base high-temperature alloys has recently received increasing attention. The term "stability" covers the requirement that structure should not change during prolonged exposure under stress at elevated temperatures, with the resultant, concomitant, and more important, factor of ensuring that the properties of the alloys shall not change in a drastic or unpredictable manner during exposure under service conditions. Since the high temperature properties of nickel-base alloys are dependent on the presence, in the structure, of phases precipitated from solid solution, some form of structural change under service conditions is virtually unavoidable. In seeking to achieve structural stability the principal aim is therefore to ensure that the structural changes which can occur do not seriously impair the properties of the material, thus preventing achievement of the desired behaviour especially when such properties must be maintained over long periods. Particularly important is the prevention of any structural change which could cause so marked a change in properties that catastrophic failure could ensue.

Carbides, and the so-called  $\gamma$ -prime phase, based on  $\text{Ni}_3\text{Al}$ , which are structural features common to most nickel-base superalloys, are intentionally formed to achieve high-temperature creep-rupture and tensile strength. Additionally, in certain alloys of comparatively high iron or chromium content, or in those in which high levels of  $\gamma$ -prime forming elements, niobium, titanium and aluminium, or high levels of solution-strengthening elements such as molybdenum, tungsten, are incorporated, with the aim of improving creep-rupture properties, certain sigma-type phases, which are not essential, may occur. Each of these structural features influences properties, to varying degrees. For example, the initial form and distribution of carbides and  $\gamma$ -prime phase, and changes in these phases due to continued precipitation and growth during service, may greatly influence properties, whilst formation of sigma-type phases usually results in marked reduction in ductility and frequently causes reduction in stress-rupture strength.

This paper describes examples of serious impairment of properties caused by structural changes of such types and exemplifies the effects of alloy composition and heat-treatment on these changes. The observations reported are based on the results of research carried out to develop improved nickel-base alloys for use in a wide range of high-temperature service: the cases cited refer to economically attractive iron-rich alloys showing good creep-rupture properties in very-long-time service temperatures around  $1200^\circ\text{C}$ , to alloys

characterized by very high tensile and creep strength at temperatures around 1400°F, e.g., for gas-turbine discs and sheet components, and to high-strength wrought and cast alloys capable of operating at temperatures above 1850°F.

#### MEDIUM-STRENGTH WROUGHT IRON-NICKEL-CHROMIUM ALLOYS

With the aim of developing iron-nickel-chromium-base alloys to their maximum potential, thereby providing economically attractive materials having strengths intermediate between those of conventional stainless steels and nickel-base superalloys, attention has been given to the effects of compositional variations on the stress-rupture properties, at 1200-1400°F, and on impact strength after long-time exposure at these temperatures, of alloys within the basic composition range 15-25%Cr, 35-50%Ni, Bal Fe. The stress-rupture strength of alloys of this type is significantly improved by additions of titanium, aluminium and niobium, in various combinations which result, at the highest levels, in precipitation of  $\gamma$ -prime, and also by addition of molybdenum or tungsten. Each of these elements, however, tends to promote formation of sigma-type phases, particularly in the iron-rich basic compositions considered in this paper.

Comparative examination of alloys containing up to 4% niobium, 3% titanium, 3% aluminium, 3% tungsten and 5% molybdenum, by room-temperature Charpy impact tests on forged-bar samples after exposure under various conditions, has established a relation between impact energy and an empirical expression defining alloy-composition: this interrelationship is illustrated in Figure 1. Within the limits of the composition ranges examined, it appears that this relationship applies to material both in the solution-treated condition (1 hour at 1830°F) and after prolonged exposure at 1200°F. The drop in impact value of material in the latter condition is most significant for alloys having the highest chromium content and the highest levels of hardening elements. As implied by the empirical expression defining alloy-composition, the principal strengthening elements, niobium, titanium and aluminium, have more pronounced effects than others on reduction of impact strength after exposure, although on the basis of the quantitative system for predicting stability developed by Boesch and Slaney<sup>(1)</sup> and Woodyatt, Sims and Beattie<sup>(2)</sup>, these elements show less tendency to promote formation of sigma-type phases than do chromium, molybdenum and tungsten. These observations suggest that the important aspect of freedom from embrittlement is dependent not only on preventing formation of sigma-type phases but also on other structural features of the alloy which can influence the sensitivity of properties to any sigma-type phases formed, since the results obtained appear to indicate that increasing amounts of  $\gamma$ -prime precipitate, resulting from increases in titanium, aluminium and niobium contents, not only cause some reduction in impact strength per se, but also render the impact properties of the alloys more sensitive to the presence of sigma-type phases.

Within the ranges of composition examined, stress-rupture strength at 1200°F, for lives up to 1000 hours, was progressively raised by increasing niobium, titanium and aluminium, and although after prolonged exposure at 1200°F impact energy was correspondingly reduced, rupture life continued to improve with alloy content, even when very low impact energies of about 5 ft. lbf. were obtained. This effect is illustrated in Figure 2, which shows stress/log time plots at 1200°F for 40% Ni, 24%Cr, Bal Fe base alloys of varying Nb+Ti content, together with the Charpy impact values determined on forged bar heat-treated 1 hour at 1830°F, cold-rolled 25%, and exposed for 1000 hours at 1200°F. A noticeable feature of these results is that although short-time rupture strength is markedly increased as niobium and titanium contents are increased, and hence impact energy is decreased, the slopes of the stress/log time plots are also significantly increased. It thus appears that in long-time strength the leaner alloys offer advantages over the most highly alloyed materials, which tend to embrittle to a far greater degree. However, it is not certain whether the greater fall in rupture strength with longer time, observed for the most highly alloyed materials, is due to formation of embrittling phases or whether this effect can be ascribed to the greater degree of supersaturation of the principal strengthening  $Ni_3(Nb\ Ti)$  phase in these materials, as postulated by Konilov, Pryankline and Oshimkova<sup>(5)</sup>. Figure 3 illustrates changes in stress-rupture strength and room-temperature impact energy for two iron-chromium-nickel-molybdenum-base alloys after exposure at 1200°F. The titanium and aluminium contents of the two materials were closely similar, but the proportions of nickel, chromium and molybdenum, differed sufficiently to produce differences in susceptibility to sigma-phase formation and marked differences in the degree of embrittlement. Holding times up to 12,000 hours produces little significant difference in stress-rupture strength, although for one alloy impact energy was reduced to 5 ft. lbf. or less by exposure for 5,000 hours or longer, and in that case approximately 3% of sigma phase was identified in the structure, whereas, in similar conditions, the other alloy retained an impact energy of approximately 30 ft. lbf. and was free from sigma phase. In these alloys, therefore, it would appear that formation of sigma phase has little effect on stress-rupture properties.

The principal findings from this research, illustrated by the above examples, suggest that the extent to which improvements in stress-rupture strength achieved by alloying additions can be employed is governed by the importance of avoiding embrittlement under rapid rates of strain. Structural changes which result in instability in impact properties do not always cause instability of stress-rupture properties.

## HIGH-STRENGTH WROUGHT NICKEL-BASE ALLOYS

The majority of wrought nickel-base alloys, used in highly stressed high-temperature applications such as gas turbine components, have tensile and stress-rupture strengths which fall within the ranges indicated in Figure 4. It has been possible, within these strength ranges, to develop nickel-chromium-base  $\gamma$ -prime-strengthened alloys, in some cases containing cobalt and molybdenum, without general resort to compositions which are susceptible to formation of embrittling sigma-type phases, but the large amounts of  $\gamma$ -prime forming elements necessary in alloys required to meet the very highest levels of stress-rupture strength now specified can cause formation of sigma-type phases unless the basis alloy composition, particularly the chromium and molybdenum contents, is suitably adjusted and controlled. For the most part, however, any structural changes and associated changes of properties in alloys within these strength ranges are concerned with  $\gamma$ -prime phase and carbides, which are essential constituents.

### Effects of Carbides

Two alloys (A and B) in Table I, illustrate the effects, on room-temperature hardness and impact strength, of compositional changes required to improve the stress-rupture strength of alloys depending essentially on increases in the amount of  $\gamma$ -prime-forming elements, titanium and aluminium, with corresponding adjustment of carbon content and solution-hardening elements. Alloy A (3.71% total Ti + Al), which has stress-rupture strength toward the lower end of the range shown in Figure 4, exhibits, before exposure, an impact-energy value considerably higher than that of Alloy B (total 5.84% Ti + Al), which has rupture strength at the high end of the range. This effect is attributed partly to the difference in the amount of  $\gamma$ -prime precipitated in the respective alloys, but the larger amounts of grain-boundary carbide precipitated in Alloy B are probably mainly responsible for its lower impact value. The influence of variation in the amount of grain-boundary carbide precipitation is demonstrated by comparing results for Alloy A in the two conditions of heat-treatment. Heating at 1652°F during the three-stage heat-treatment (1976°F + 1652°F + 1292°F) caused increased precipitation of grain-boundary carbides, as compared with that resulting from the two-stage treatment (1976°F + 1292°F), and impact value was correspondingly reduced, from about 68 ft. lbf. to 44 ft. lbf. Exposure at 1200°F for times up to 10,000 hours caused reduction in room-temperature impact value for Alloy B and for Alloy A. However, whereas the impact values for Alloy B and for Alloy A, heat-treated by the three-stage treatment remained relatively constant beyond 1000 hours' exposure, those of Alloy A, after the two-stage treatment continued to fall progressively with increasing time and after 10,000 hours' exposure were actually lower than those of corresponding samples initially treated by the three-stage method. Comparison of hardness after exposure (governed mainly

by precipitation of  $\gamma$ -prime) with impact values suggests that the effects observed are due to some other structural change, particularly in Alloy A which had undergone the two stage treatment. In that case the progressive fall in impact energy is attributed to continued precipitation of grain-boundary carbide, which, by virtue of the low exposure temperature, occurs as fine continuous grain-boundary films, in contrast to the large discrete particles produced at the higher temperatures involved in the three-stage treatment and also in the treatment applied to Alloy B.

Further evidence of the effect of heat treatment and carbide structure, on stability of properties, is shown by results obtained from room-temperature tensile tests on samples initially heat-treated by the two- and three-stage methods, and exposed, under creep conditions, at 1200°F and 1600°F.: see Figure 5. In each case the creep tests were discontinued at or before 0.5% strain, to minimize the possibility of subsequent tensile properties being severely affected by formation of cavities. In material treated by the three-stage method creep at both test temperatures had little effect on tensile elongation, and for material treated by the two-stage method it was only after creep at 1200°F that the tensile elongation value was progressively reduced to very low levels. The relatively slight effect on elongation after creep at 1600°F is considered to be due to the fact that the optimum carbide structure was quickly developed, during the early stages of creep testing at that temperature.

These examples demonstrate the importance of stabilizing the carbide structure before service, by applying a heat-treatment which will precipitate grain-boundary carbides in the form of relatively large discrete particles. This precaution is particularly important for material to be used at relatively low service temperatures, because although the initial ductility or impact value may thus be slightly lowered, the values so obtained will be maintained in service for longer periods.

It has also been found that treatments of the three-stage type used for Alloy A, which stabilize the structure of the alloys and minimize further precipitation of the principal phases during service or testing, lessen notch-weakening in stress-rupture tests and reduce susceptibility to crack during heat-treatment after welding. Each of these effects may be regarded as generally associated with changes in properties at high temperatures under conditions of stress concentration. Both these features are of considerable practical importance.

The effectiveness of a three-stage treatment in overcoming notch-sensitive behaviour in stress-rupture tests at 1112°F is illustrated in Figure 6, for a cobalt-free alloy which is otherwise identical in composition with Alloy A. Stresses at which stress-rupture tests on notched bars were made are plotted against the ratio of that stress to the stress giving a corresponding life for unnotched bars. The time-scale, in association with the stress-scale, indicates the mean lives obtained for unnotched bars treated by the two stage method, and shows the times up to which the absence of notch-sensitivity has been determined.

Quantitative indication of susceptibility to cracking during post-weld heat-treatment was obtained by heating bar samples from room temperature, under a condition of constant strain, until failure occurred or until the initially imposed stress was completely relaxed. Maximum strain imposed at room temperature tolerable without failure of the sample during heating is taken as a comparative measure of resistance to this type of failure. Such tests, made on bar samples of the alloy referred to in Figure 6, show maximum tolerable strain of 9% for material heat-treated for 1 hour at 2100°F, and water-quenched, whereas material treated 1 hour at 2100°F, furnace-cooled to 1832°F and held at that temperature for 4 hours before water-quenching tolerated a strain of 26%. The structures obtained for material in each condition of heat-treatment, before and after heating under strain, (shown in Figure 7) indicate that during test carbides precipitate preferentially on pre-existing carbides produced by the furnace-cooling treatment, but that without that intermediate treatment fine carbides are precipitated on slip planes, and reduce ductility much more severely.

#### EFFECTS OF $\gamma$ -PRIME

The principal strengthening phase in high-temperature nickel alloys is based on compounds of the form  $Ni_3X$ , where X may be titanium, aluminium or niobium, or a combination of these elements. The properties obtained obviously depend on the volume fraction of the  $Ni_3X$  phase precipitated and also on the composition and structure of the phase, which govern its morphology and rate of growth.

A review has been made by Schwaab and Hagen<sup>(4)</sup>, of the extensive metallographic studies which have been carried out on nickel-chromium-base alloys hardened with aluminium and titanium. In general, development of such alloys has indicated that those in which the Ti/Al ratio ranges up to approximately 4/1 precipitate  $\text{Ni}_3(\text{TiAl})$  with a stable face-centred cubic structure, which remains unchanged after prolonged high-temperature exposure. The only form of instability expected with respect to this phase is therefore that of rate of particle-growth and associated over-ageing effects. These changes, in turn, are influenced by variations in alloy composition and resultant variations in mismatch between matrix and precipitate. Such structural changes are, however, sluggish, and do not cause serious changes in properties.

In alloys for components such as gas-turbine discs and sheet material the demand is for high tensile strength at temperatures up to about 1200 or 1400°F and very good workability, which imposes limits on the amount of titanium and aluminium which can be added to increase strength. This problem has prompted investigation of compositions containing modified hardening phases of  $\text{Ni}_3\text{X}$  type composed principally of niobium or titanium, and each of these elements, particularly niobium, has been found effective. Characteristic effects of varying the proportions of niobium, aluminium and titanium are illustrated in Figure 8. Strength at temperatures below about 1400°F is increased by use of niobium in preference to combined additions of titanium and aluminium, but fall in strength at higher temperatures is generally more rapid. Metallographic studies of these and similar alloys strengthened with niobium alone has shown that plates of  $\text{Ni}_3\text{Nb}$ , an ordered body-centred tetragonal phase, are precipitated: see Figure 9a. This phase is initially coherent with the matrix, but it overages comparatively quickly, probably because of the greater lattice mismatch between the matrix and the C-axis of the body-centred-tetragonal unit cell. In alloys strengthened with titanium alone the hardening phase consists initially of particles which have an ordered face-centred -cubic crystal structure. Thin-foil microscopy indicates that initially this precipitate is coherent with the matrix, but that at temperatures above about 1400°F overageing is rapid, and needles of  $\text{Ni}_3\text{Ti}$ , with close-packed hexagonal crystal structure, are formed: see Figure 9b. Additions of aluminium to alloys rich in niobium or titanium inhibit formation of these needle-or plate-like precipitates, in favour of spherical precipitates of the face-centred-cubic phase. This retards overageing, and produces properties intermediate between those characteristic of niobium-hardened alloys and those hardened by the stable  $\text{Ni}_3(\text{TiAl})$  phase.



The general conclusion is, therefore, that whereas, for a given level of hardening, additions forming the  $\text{Ni}_3\text{Ti}$  or  $\text{Ni}_3\text{Nb}$  phase, greatly improve strength at temperatures below about  $1400^\circ\text{F}$ , at higher temperatures greater strength and more stable properties are obtained when sufficient aluminium is present to promote formation of precipitates of face-centred-cubic structure having a smaller lattice mismatch with the matrix.

#### HIGH-STRENGTH CAST NICKEL-BASE ALLOYS

One group of high-strength alloys designed for use in the cast state is based on a nickel-chromium-cobalt-molybdenum matrix in which  $\gamma$ -prime strengthening is achieved by additions of titanium and aluminium, present in greater total content than that used in the strongest wrought alloys. Investigation of the effects of compositional variations on the stress-rupture properties of 10% Co, 10% Cr Bal Ni alloys containing varying molybdenum and additions of titanium and aluminium in roughly equal proportions, showed that the extent of  $\gamma$ -prime strengthening was limited by formation of sigma phase: see Figure 10. The close relation between the discontinuous line representing the contour of maximum stress-rupture life (Figure 10b) and the sigma-phase boundary (Figure 10a) indicates that increase in titanium and aluminium contents is effective in lengthening stress-rupture life only up to the amounts causing formation of sigma phase. Further increase is detrimental. During that compositional survey it became apparent that stress-rupture strength was greatest in an alloy containing molybdenum 4%, titanium 5%, aluminium 5%, which was free from sigma phase in the as-cast condition. During exposure at elevated temperatures, however, progressive precipitation of sigma phase occurred: the effect was most rapid within the range  $1470$ - $1650^\circ\text{F}$ , and long-time exposure at temperature resulted in substantial fall in stress-rupture strength. Formation of the precipitate was suppressed, and long-time stress-rupture properties were thereby improved, by slight reduction in titanium content; see Figure 11. Metallographic examination of test specimens containing 5.2% titanium revealed that precipitation of sigma phase had begun after 310 hours under test and that in the specimen exposed for 1232 hours a considerable amount was present. It is evident, therefore, that an appreciable amount of sigma-phase was already present when the drop in rupture strength occurred after approximately 750 hours. Although the alloy containing 4.6% titanium showed no corresponding fall in rupture strength, appreciable amounts of sigma phase were detected in specimens tested for 1719 and 8750 hours. These observations indicate that under conditions of low strain-rate a certain proportion of sigma phase which, in alloys of this type, occurs in the form of platelets, can be tolerated without risk of instability occurring after long times at elevated temperatures. It seems improbable, therefore, that the presence of sigma phase per se is wholly

responsible for reduction in rupture strength. In an attempt to explain the observations made it is postulated that precipitation of sigma phase progressively depletes the matrix of alloying elements, notably chromium, molybdenum and titanium, which increases its solubility for titanium and aluminium, and thereby reduces the extent of  $\gamma$ -prime strengthening in areas adjacent to sigma-phase particles. In the early stages small compositional changes resulting from these structural changes will have little effect on rupture strength, but with continued depletion of the matrix substantial reduction in rupture strength will eventually occur. The essentially parabolic relationship between hardener-content and stress-rupture life found in earlier alloy development studies<sup>(5)</sup> lends support to this hypothesis.

Whilst it has been demonstrated that under conditions of slow-strain the presence of sigma phase in alloys of the former type does not necessarily result in instability, impact strength is lowered by even small amounts of that phase. Hence, in applications which demand maximum retention of both stress-rupture and impact strength, it is necessary to make compositional modifications which will completely inhibit precipitation of sigma. Figure 12 (upper portion) illustrates the effect of variations in titanium and aluminium contents on the stress-rupture life of a 10% cobalt-10% chromium-4% molybdenum Bal Ni alloy, demonstrating the possibility of maintaining a high level of rupture strength in alloys of reduced titanium content, provided that a compensating increase in aluminium is made. These compositional modifications result in virtual freedom from sigma-phase precipitation during long times of exposure at elevated temperatures and thereby secure maximum retention of impact strength. In the lower portion of Figure 12 the two shaded areas define compositions of alloys which, combine a stress-rupture life of more than 100 hours at 13,400 p.s.i. and 1922°F with impact strength above 35 ft. lbf. after exposure for 1000 hours at 1562°F. The alloy containing 3.5% titanium and 5.8% aluminium, within the overlapping portion of the two shaded areas, satisfies both criteria. The fall in impact strength after exposure, which becomes pronounced as the titanium content is further reduced to below 3%, is attributable to precipitation of carbides at grain boundaries.

A higher level of stress-rupture strength, required in some more critical applications, is provided by alloys of lower chromium content, in which a higher degree of solid-solution strengthening is achieved by substantial additions of tungsten in combination with other solid-solution hardening elements, notably molybdenum, niobium and tantalum.  $\gamma$ -prime strengthening is achieved primarily by additions of aluminium, and, in some alloys, by aluminium + titanium. Alloys of this type, although not susceptible to sigma-phase precipitation, generally exhibit lower impact strength in the as-cast condition than the class of cast alloy discussed earlier. Impact strength also tends to fall during prolonged exposure at elevated

temperatures, as a result of precipitation of grain-boundary carbide. Although the presence of carbides is usually considered essential for maximum stress-rupture strength, a marked increase in impact strength, with only slight reduction in stress-rupture strength, has been achieved by lowering the carbon content of a 6%Cr, 11%W, 2%Mo, 1.5%Nb, 6%Al, Bal Ni alloy from 0.13% to <0.03%: see Figure 13. The low-carbon alloy shows no tendency towards loss of impact strength after exposure at 1562°F for times up to 3,000 hours, and the reduction in carbon content virtually eliminates the grain-boundary carbide network and increases the amount of  $\gamma/\gamma'$ -eutectic: see Figure 14.

Gradual increase in the overhaul times for civil aircraft engines is a further factor which has focussed attention on the long-term strength capability of new alloys in the aircraft field. In general, the nickel-chromium-tungsten-base alloys tend to exhibit steeper stress vs. rupture life characteristics than the nickel-cobalt-chromium-molybdenum types and, when their higher density also is taken into account, as for example in rotating blades, the former alloys can have a lower strength capability in times longer than about 1000 hours: see Figure 15. Investigation of the effects of minor compositional variations e.g. addition of zirconium and boron on the long-time stress-rupture properties of a 6% chromium, 11% tungsten, 2% molybdenum, 6% aluminium Bal Ni alloy are illustrated in Figure 15. It was observed that although short-time rupture strength was increased to only a small extent, strength-capability, in times up to 1000 hours or more, was significantly improved by slight reduction in zirconium content coupled with addition of boron. Even when the increased density resulting from the presence of tungsten was taken into account, the modified alloy showed a strength advantage over the 10% cobalt, 10% chromium, 4% molybdenum, Bal Ni alloy in times-to-rupture longer than 1000 hours. The role of zirconium and boron is, however, not yet fully understood. To facilitate development of such alloys, for use in critical applications where high strength over prolonged periods at elevated temperature is of paramount importance, further research is needed to gain a better understanding of the exact mechanism by which these elements influence stress-vs.rupture life characteristics.

## DISCUSSION

In general the question of stability in nickel-base high-temperature alloys can be classified into two categories, viz., instability arising from the formation of phases which are not an essential factor in achieving the principal property of creep-resistance characteristic of these alloys, and, secondly, changes in the mode and distribution of precipitated phases essential for high-temperature properties.

In category one the most important effect is produced by formation of sigma-type phases. However, in most alloys, this phenomenon is uncommon and becomes apparent only in cases where (a) in the interest of reduced cost, iron content is substantially increased, (b) where chromium content is increased, to obtain maximum resistance to hot corrosion, or (c) when the proportions of conventional strengthening elements such as titanium, aluminium, niobium, molybdenum and tungsten are raised to very high levels, to achieve maximum high-temperature strength. The need to ensure stability therefore restricts the extent to which desirable improvements can be achieved in each of these directions and this becomes increasingly significant with the trend towards lengthening of service time.

In assessing the problems involved due consideration should, however, be given to the precise effects of the respective structural changes and, thus, the extent to which they present a barrier to the effective use of an alloy in a particular application. In general, the major effect of sigma-type phases appears to be to reduce ductility (impact-resistance) under high rates of strain but in some instances this effect is indeed no greater than that produced by other essential phases in alloys which are well established in engineering use. Provided the amount of sigma-type phases formed is not excessive, their effect on stress-rupture strength can often be negligible. Clear appreciation of the service conditions involved and the significance, in known conditions, of particular properties, may therefore facilitate exploitation of higher creep strength, by permitting use of alloys which are subject to some change in a less important property.

Changes in properties resulting from structural effects involving phases essential in the alloy can be as significant as formation of undesirable phases. In particular, continued precipitation of carbides under conditions of stress, during fabrication or service, can result in marked reduction in ductility. Instability of the principal strengthening phase,  $Ni_3(Ti Al Nb)$ , in the form of changes in crystal structure, diminished cohesion with the matrix lattice, and overageing, may limit the strength achieved in long times or at higher temperatures. However, these effects can usually be avoided or minimized by selection of suitable composition and heat-treatment, as indicated by some of the results quoted above. Maximum strength is

usually achieved by using an alloy in a condition of heat-treatment which leaves it susceptible to structural changes of the chief phases, and resultant reduction in ductility during prolonged high-temperature exposure. It is generally advisable, therefore, to select a material the maximum strength potential of which is more than adequate for the application envisaged and to apply to it a heat treatment which, although lowering strength to some extent, stabilizes the precipitates sufficiently to minimize further precipitation in service.

#### ACKNOWLEDGEMENT

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#### REFERENCES

1. Boesch, W.J. and Slaney, J.S.: "Preventing Sigma Phase Embrittlement in Nickel Base Superalloys"; Metal Prog., 1964, 86, July, pp. 109-111.
2. Woodyatt, L.R., Sims, C.T. and Beattie, H.J.; "Prediction of Sigma type Phase Occurrence from Compositions in Austenitic Superalloys"; Trans. metall. Soc. A.I.M.E., 1966, 236, pp.519-527.
3. Kornilov, I.I., Pryakhina, L.I. and Ozhimkova, O.V.: "The Effect of the Time Factor on the Character of the Diagram of Composition vs. Heat-resistance for Alloys of the Five-Component System Ni-Cr-W-Ti-Al"; Issled. po Zharoproch. Splavam, Inst. Met. A.A. Baikova, 1960, 6, pp. 278-283.
4. Schwaab, P. and Hagen, K.: "Precipitation Phenomena in Nickel-Chromium Alloys with Aluminium and Titanium Additions"; Z. Metallk., 1963, 54, pp. 23-30.
5. Cook, R.M. and Shaw, S.W.k.: "Recent Developments in Cast Nickel Alloys for High-temperature Applications"; Revue Métall., 1966, 63, pp.329-338.

TABLE I

IMPACT AND HARDNESS OF TWO NICKEL-BASE ALLOYS  
AFTER EXPOSURE AT 1200°F

Alloy	Composition, wt.% *								Heat Treatment	Properties as heat-treated		Properties after Exposure at 1200°F			
	C	Cr	Co	Mo	Ti	Al	B	Zr		Izod Impact (ft.lbf.)	Hardness HV 30	1000 hours		5000 hours	
											Izod Impact (ft.lbf.)	Hardness HV 30	Izod Impact (ft.lbf.)	Hardness HV 30	
A	0.09	19.2	16.3	<0.2	2.40	1.31	0.009	0.06	8h 1976°F, a.c. + 16h 1292°F, a.c.	69, 69, 68.	344	37, 39, 42.	344	22, 23, 22.	360
									8h 1976°F, transferred to 1652°F, held 24h, f.c. + 16h 1292°F, a.c.	43, 45, 44.	295	37, 35, 34.	320	26, 27, 29.	309
B	0.15	15.3	19.7	4.9	1.23	4.61	0.008	0.10	4h 2102°F, a.c. + 16h 1922°F, a.c. + 16h 1562°F, a.c.	10, 6, 11.	364	3, 2, 3.	406	2, 2, 2.	418

\* - Balance substantially nickel  
a.c. - air-cooled f.c. - furnace-cooled

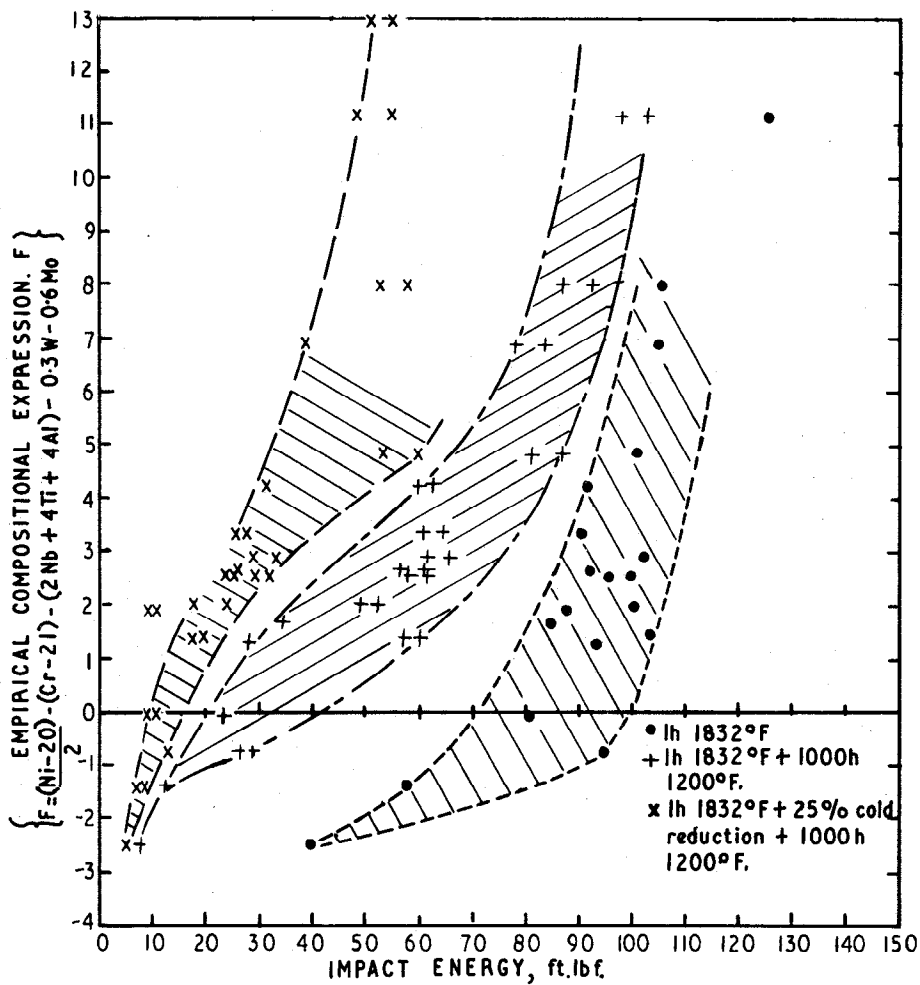


Figure 1 Relationship between composition and impact strength of wrought Fe-(39-45)%Ni-(20-25)%Cr-base alloys.

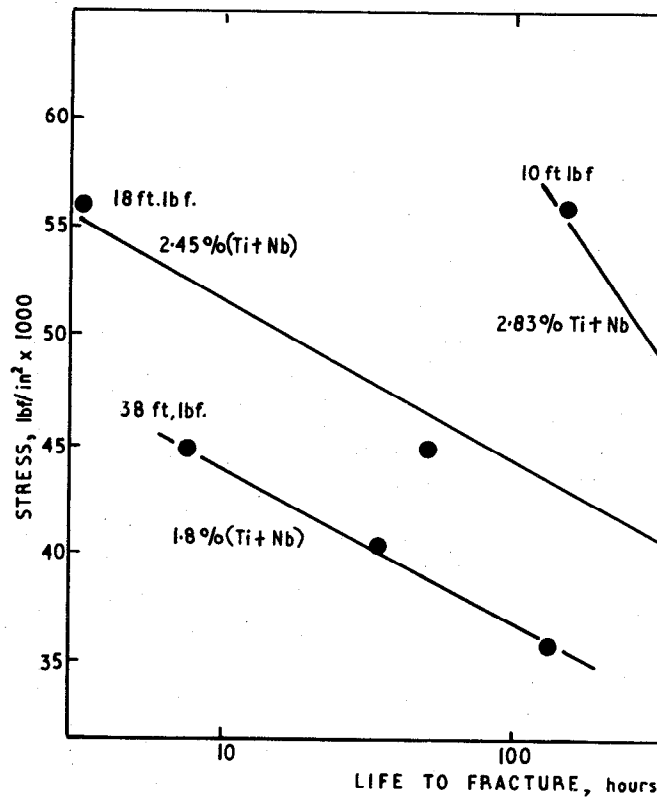


Figure 2 Influence of Ti+Nb content on stress rupture and impact strength following exposure at 1200°F base alloys. (Stress rupture tests on forged bars; Charpy-V notch impact tests on bar heat treated 25% and heated 1000h 1200°F).

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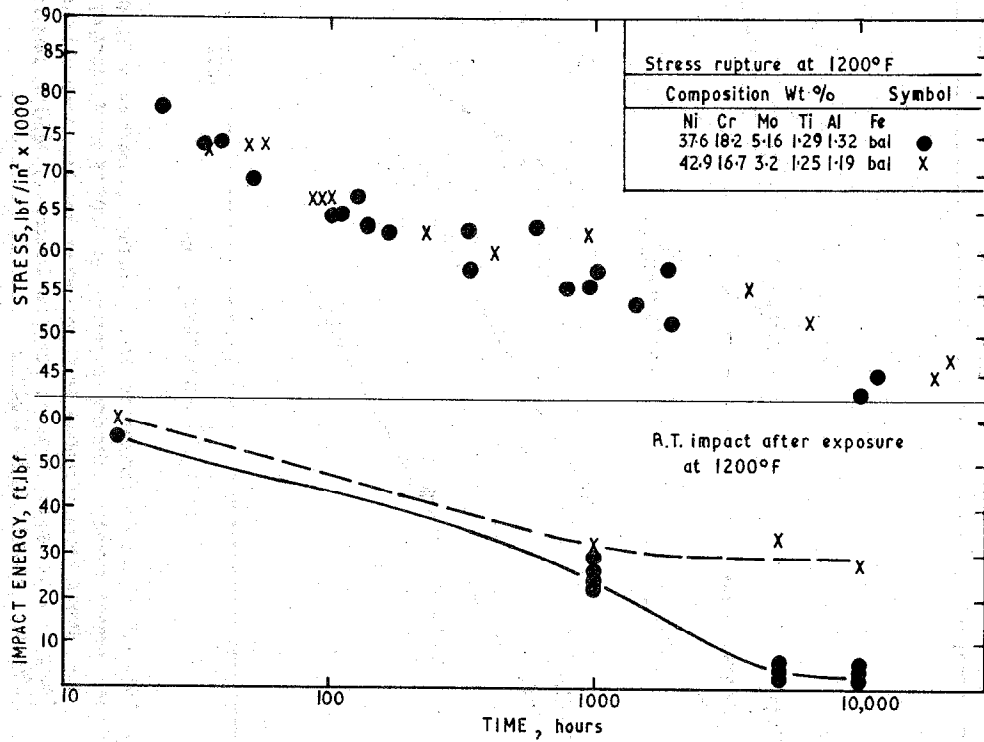


Figure 3 Comparison of stress rupture life at 1200°F and room temperature Charpy impact value after exposure at 1200°C for two Fe-Ni-Cr base alloys. (Tests made on forged bar samples heat treated initially for 8h 1830F + 16h 1290°F).

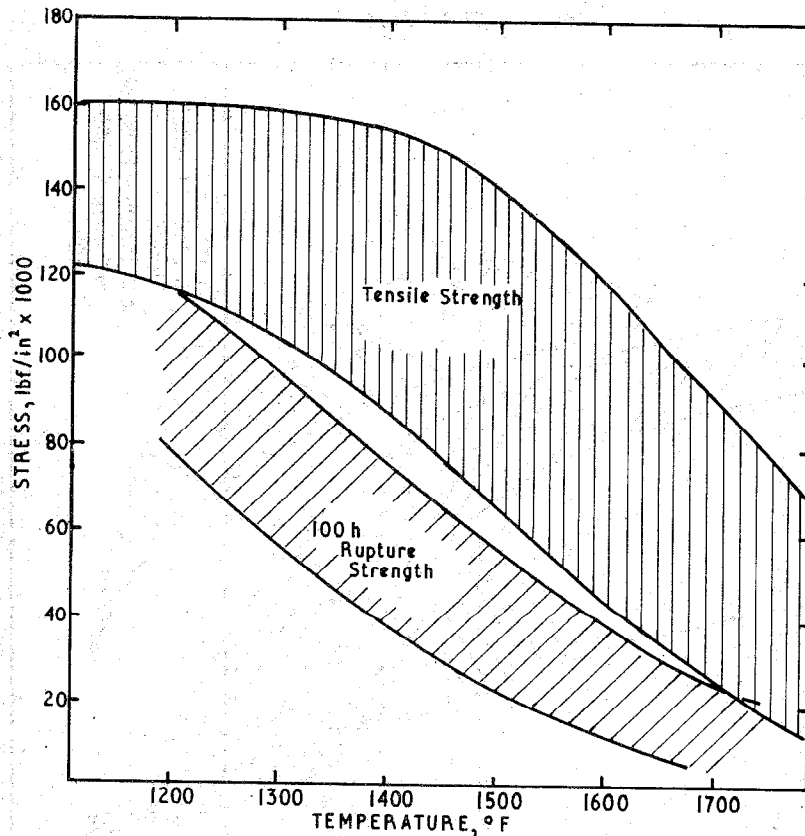


Figure 4 Ranges of tensile and stress rupture strengths for commercial wrought nickel base alloys.



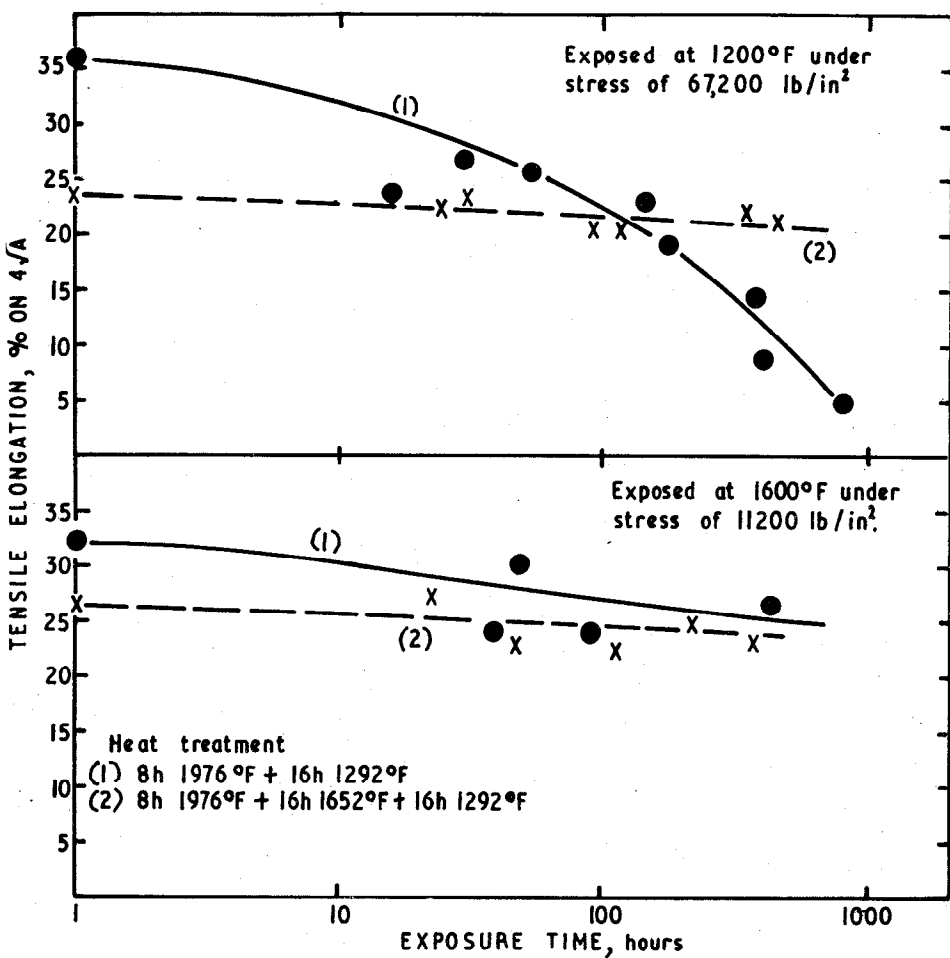


Figure 5 Effect of heat treatment on the room temperature tensile elongation following creep exposure of a wrought nickel base alloy. (Alloy A, see Table I).

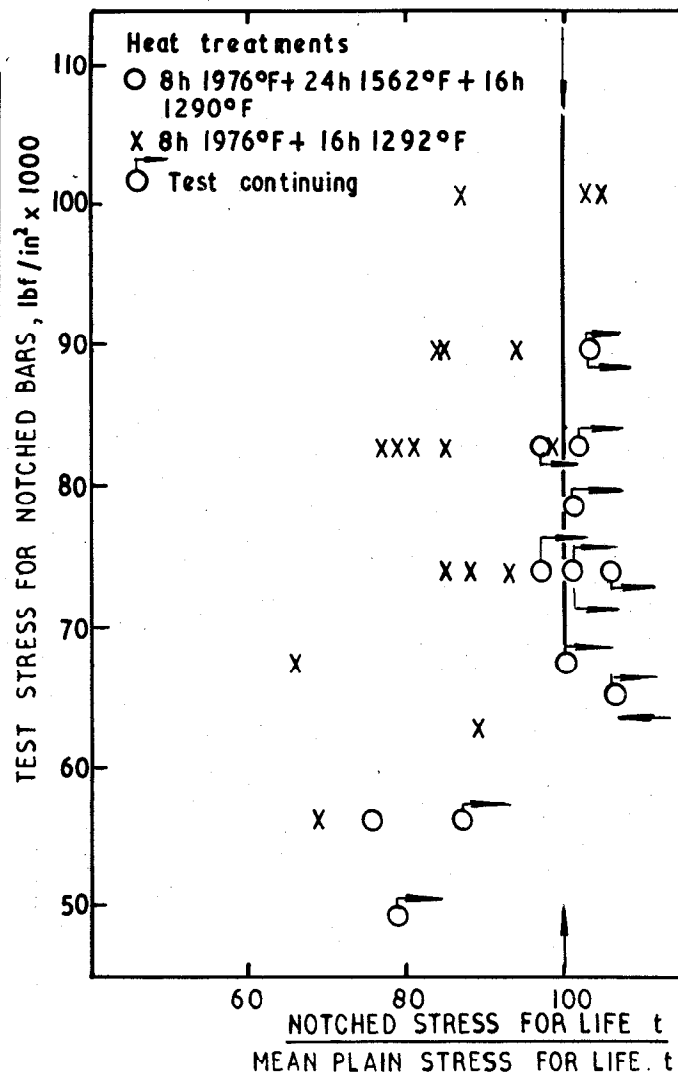
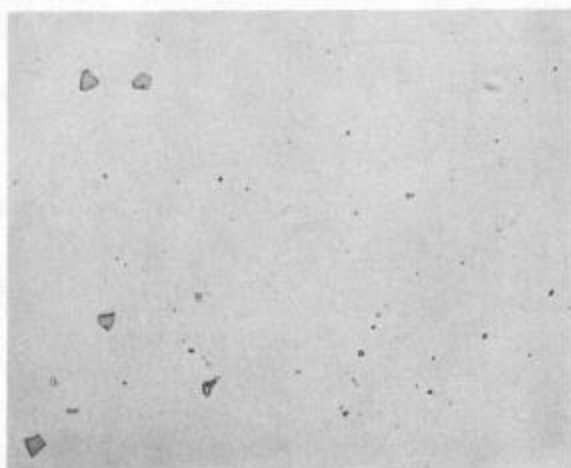
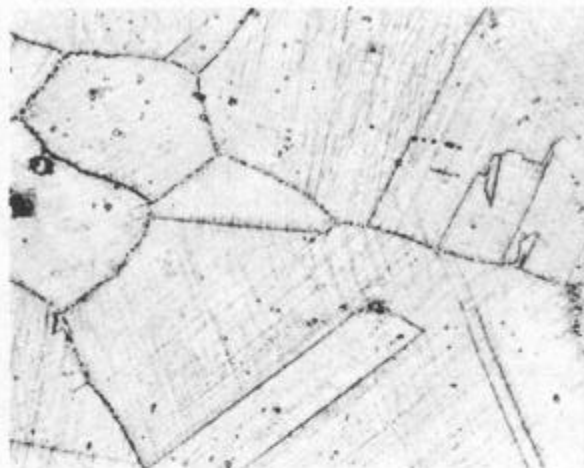


Figure 6 Effect of heat treatment on notch sensitivity of a Ni-20%Cr-2.4%Ti-1.2%Al alloy.



(a)

B. 7832



(b)

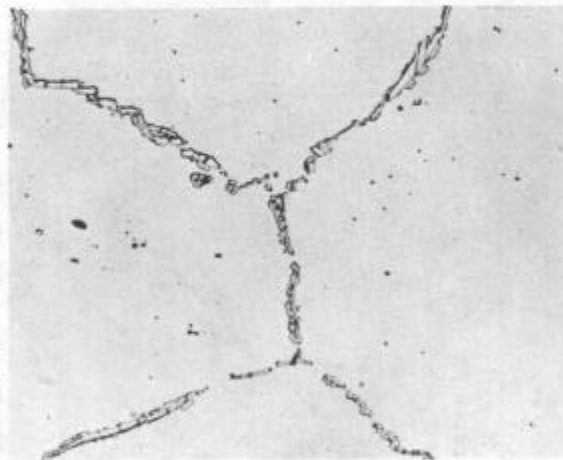
B. 8008

1 hour 2100°F water-quenched



(c)

B. 7830



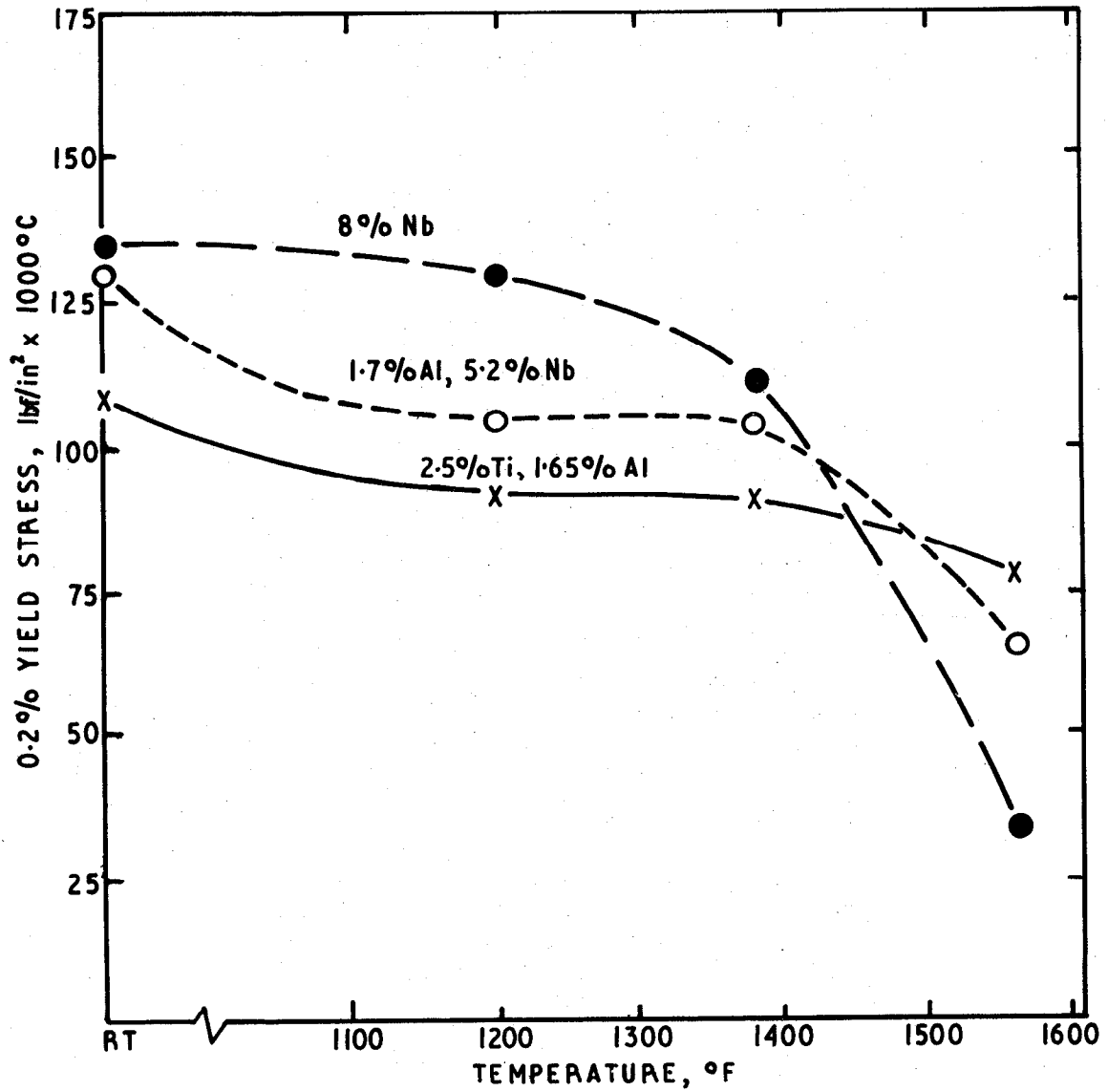
(d)

B. 8007

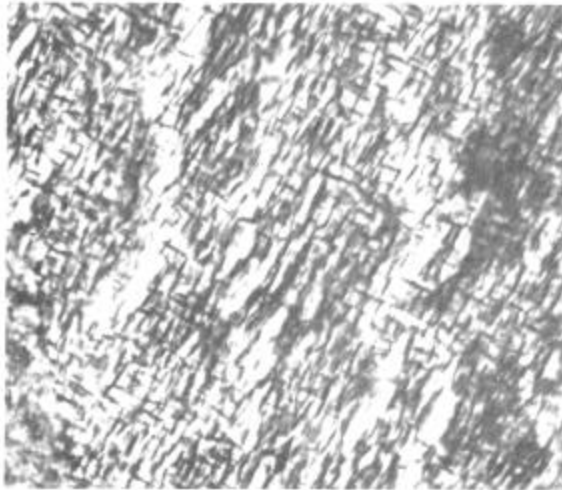
1 hour 2100°F, furnace-cooled to 1832°F held 4 hours  
and water-quenched

Figure 7.X500

Structures of a Ni, 20% Cr, 2.4% Ti, 1.2% Al alloy after  
initial heat treatment (a & c) and after heating from  
room temperature in a strained condition until failure  
occurs (b & d)



**Figure 8** Effect of different combinations of hardening elements on the tensile properties of wrought Ni-20%Cr-0.05%C alloys. (Samples heat treated 1h 2100 $^{\circ}\text{F}$  air cool + 16h 1292 $^{\circ}\text{F}$ ).



x 40,000

S. 13965



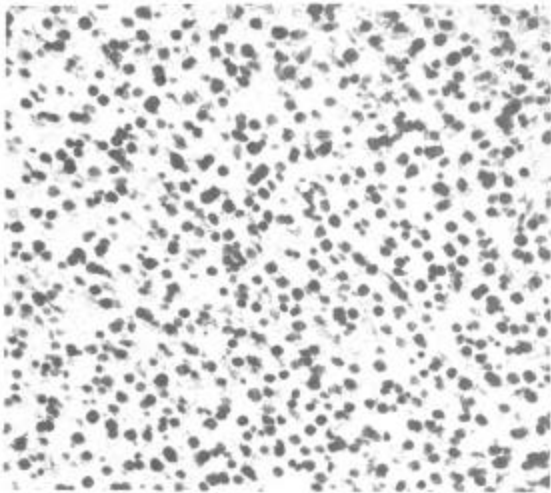
x 4,000

E. 33963

125 hours at 1200°F

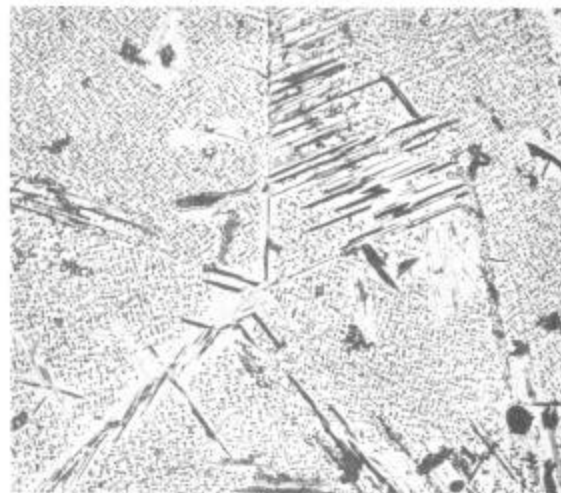
1,000 hours at 1200°F

(a) Alloy hardened with 8% niobium



x 40,000

S. 16501



x 4,000

E. 33976

25 hours at 1400°F

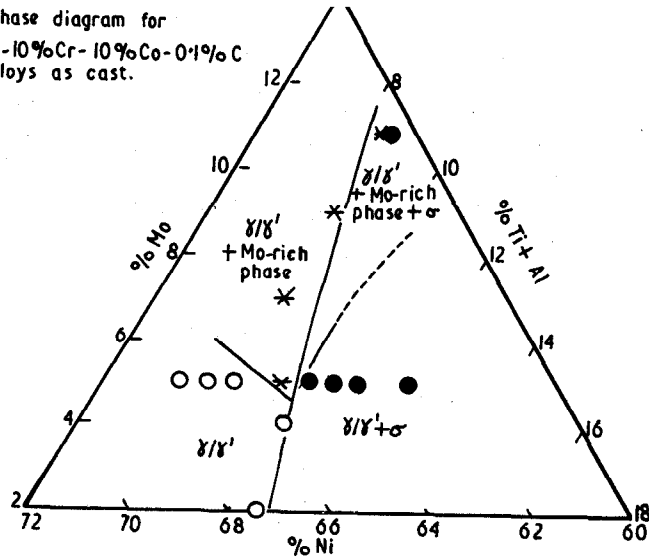
250 hours at 1400°F

(b) Alloy hardened with 4% titanium

Figure 9.

Extraction replicas from Ni-20% Cr base alloys hardened with either titanium or niobium and aged at the indicated times and temperatures.

(a) Phase diagram for Ni-10%Cr-10%Co-0.1% C alloys as cast.



(b) Stress rupture life (hours) at 15,700 lbf/in<sup>2</sup>/1868°F

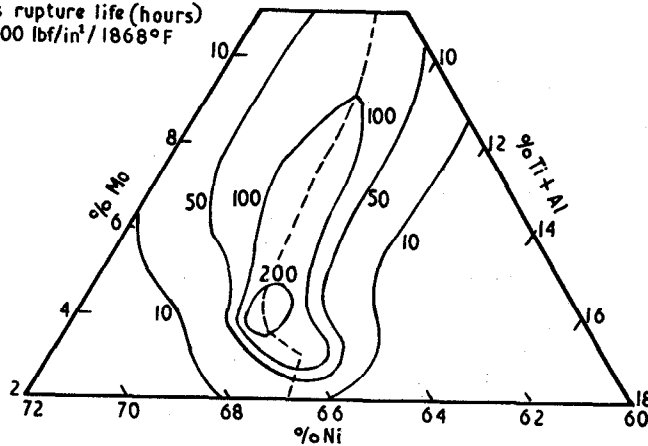


Figure 10 Effect of composition on phases present in cast structure, and on stress-rupture life.

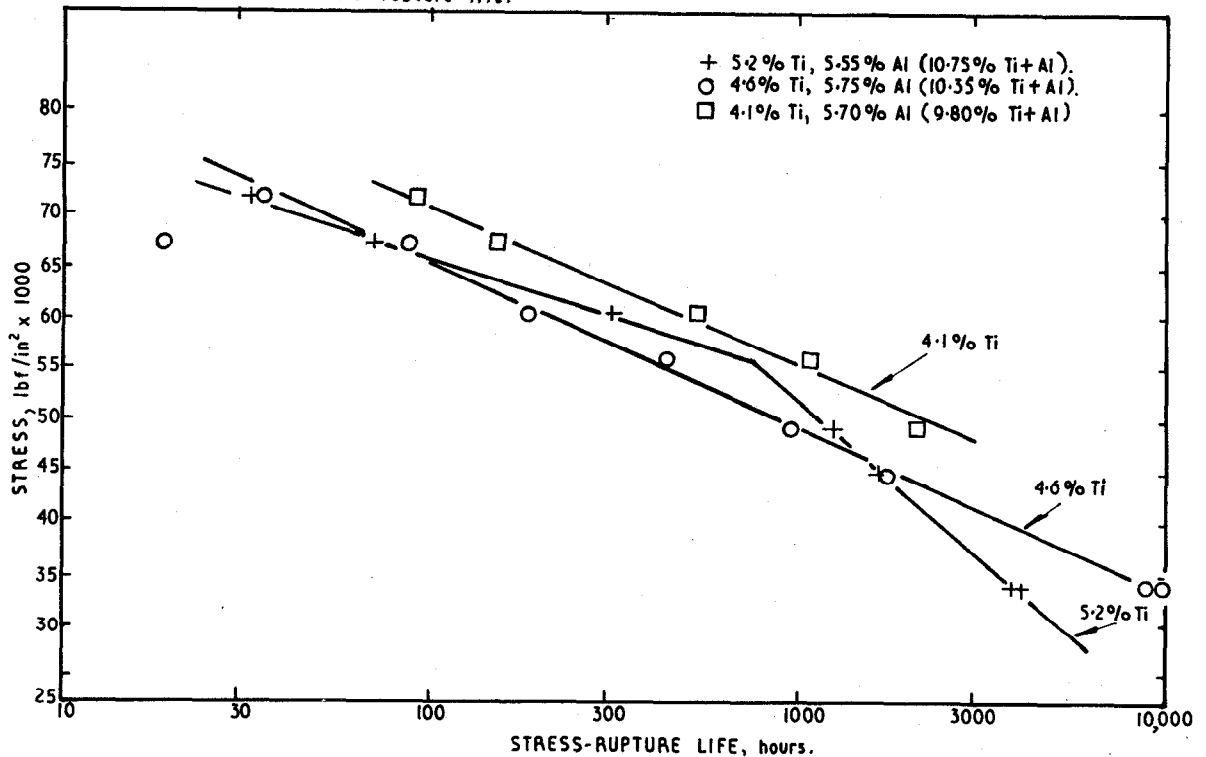


Figure 11 Effect of Ti-content on the stress-rupture characteristics of Ni-15%Co-10%Cr-3.5%Mo base alloy at 1500°F.

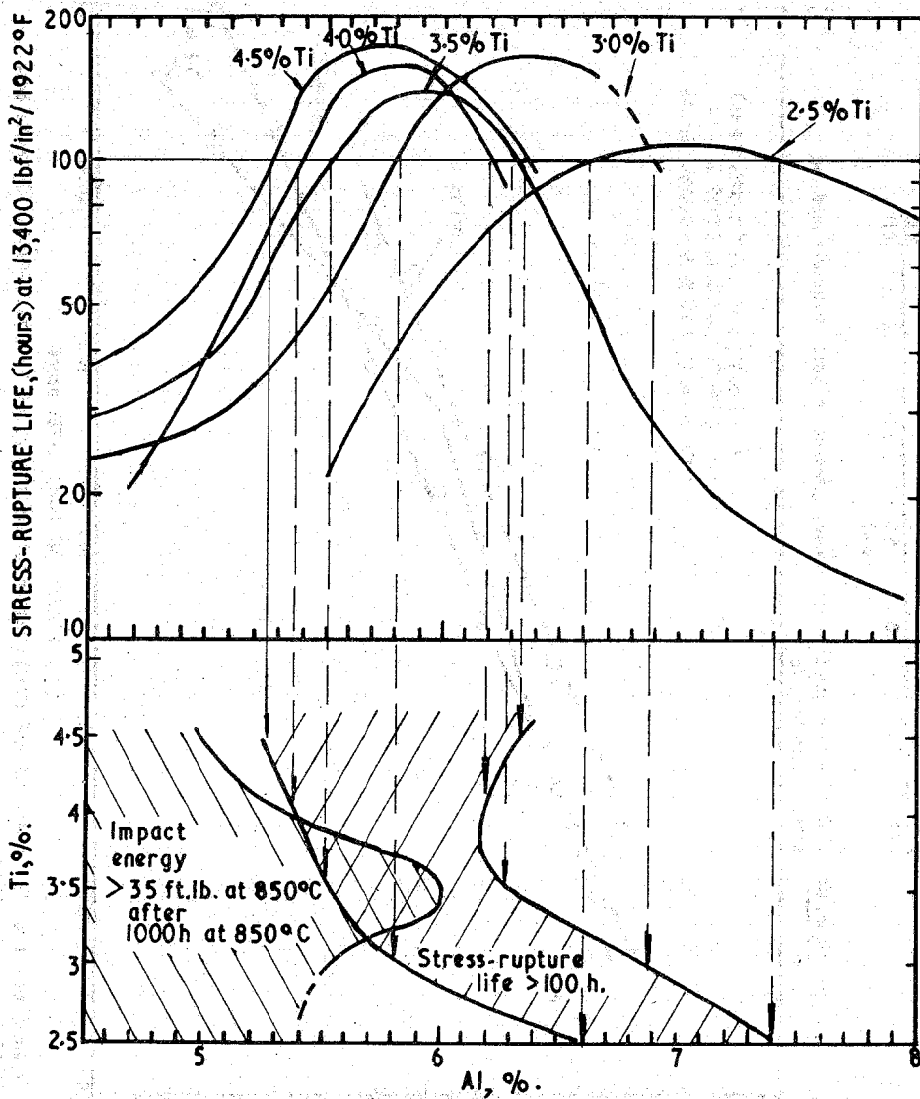


Figure 12. Effect of variations in Ti+Al content on stress-rupture life of as-cast Ni-base alloys containing Co 10%, Cr 10%, Mo 4%, C 0.1%, Zr 0.1%, B 0.01%, and on impact resistance after 1000 h at 850°C (Impact specimen: 0.45 in dia un-notched.)

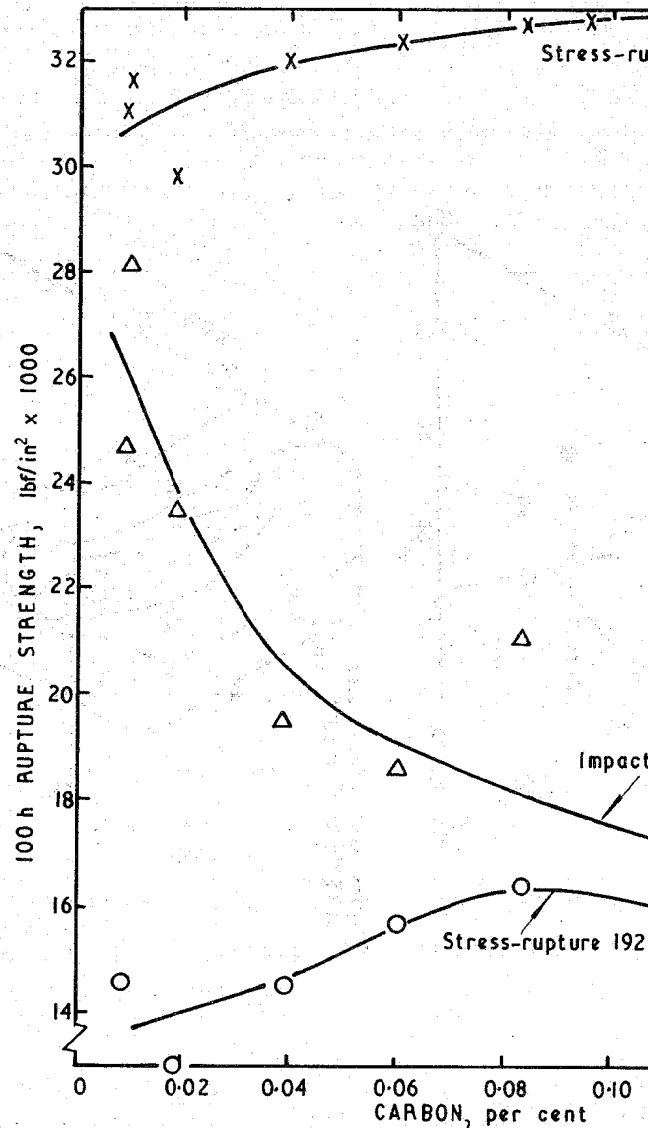
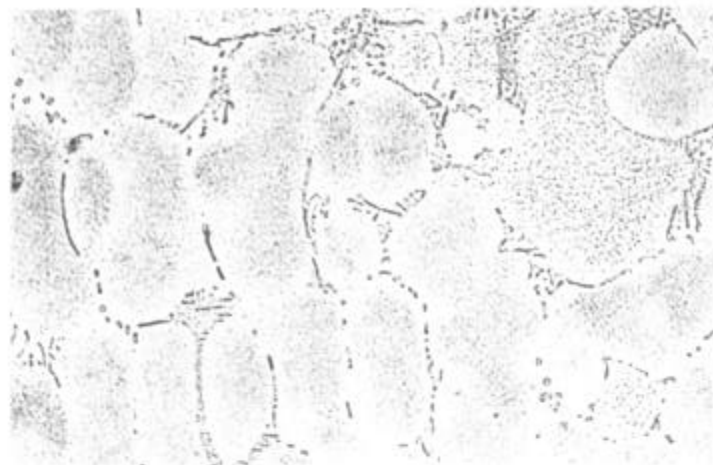


Figure 13. Effect of carbon on stress-rupture and impact resistance after 1000 h at 850°C (6% Cr-11% W-2% Mo-1.5% Nb-6% Al-0.1% C)

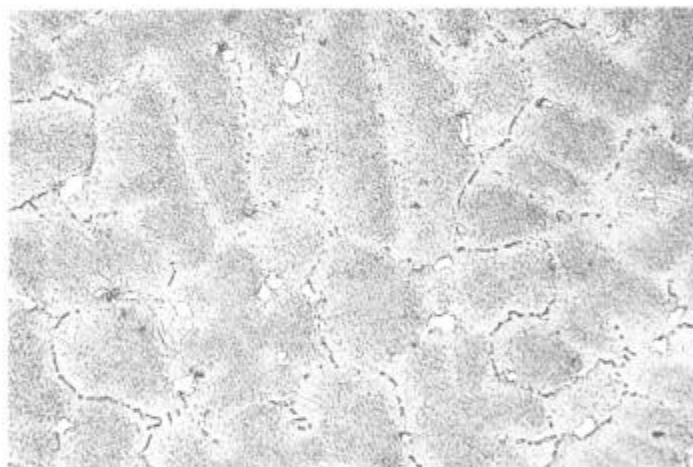


(a) 0.13% C  
As-cast impact-  
resistance at 1562°F  
of 0.45-in. (11.5mm)  
dia. unnotched bar.  
24-ft. lb (3.32 Kg.m)

x 200

37756

(b) 0.06% C  
As-cast impact-  
resistance at 1562°F  
of 0.45-in (11.5mm)  
dia. unnotched bar.  
35-ft. lb (4.85 Kg.m)



x 200

37757



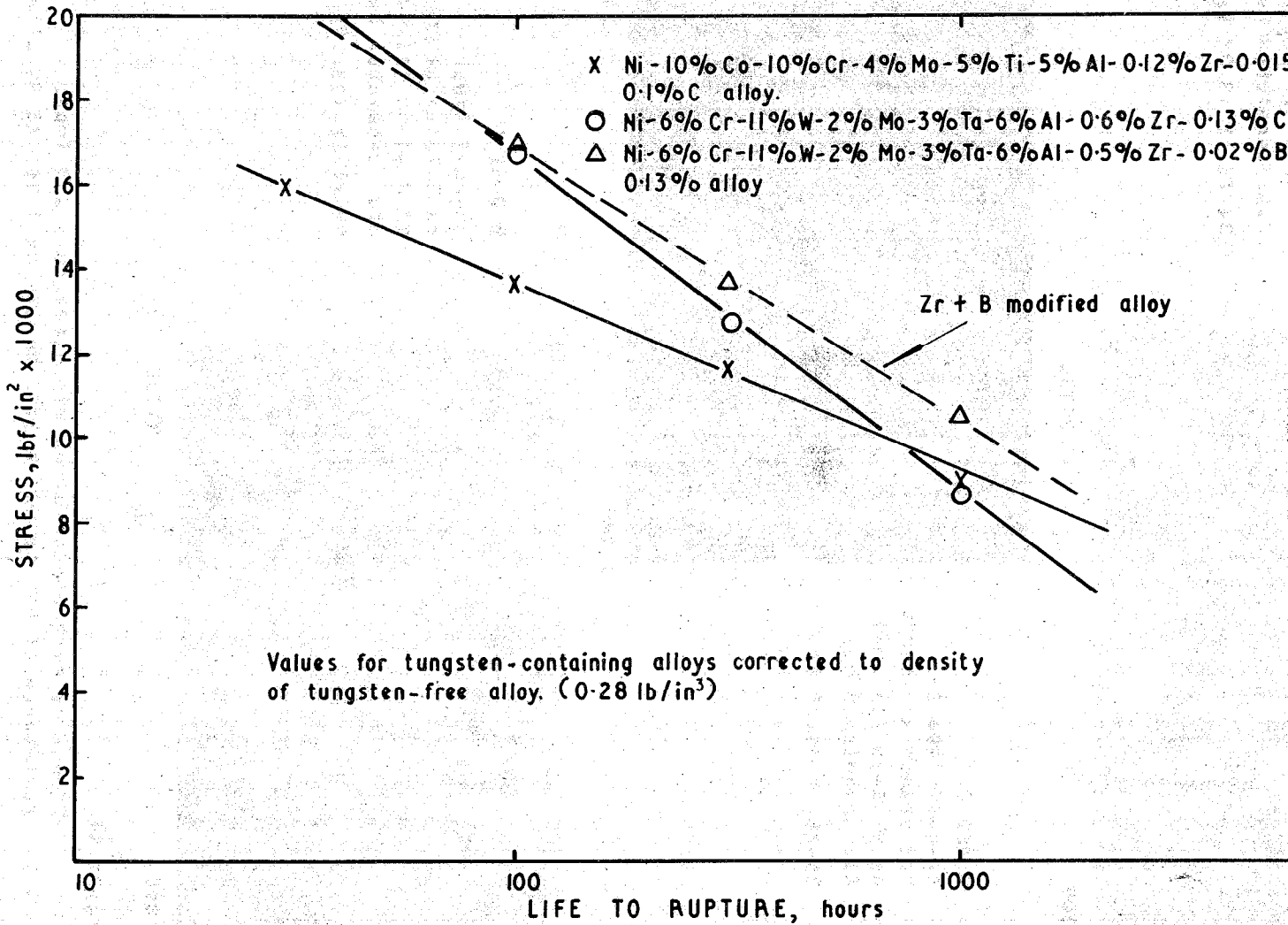
(c) 0.008% C  
As-cast impact-  
resistance at 1562°F  
of 0.45-in (11.5mm)  
dia. unnotched bar.  
82-ft. lb (12.7Kg.m)

x 200

37755

Figure 14.

Effect of carbon content on microstructure and impact-  
resistance of Ni, Cr 6%, W 11%, Mo 2%, Nb 1.5%, Al 6% alloy.



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Figure 15 Stress versus rupture life characteristics of cast nickel-base alloys at 1920°F.