

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

MEMORANDUM 4-15-59E

EXPLORATORY INVESTIGATION OF ADVANCED-TEMPERATURE NICKEL-BASE ALLOYS

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SUMMARY

An investigation was conducted to provide an advanced-temperature nickel-base alloy with properties suitable for aircraft turbine blades as well as for possible space vehicle applications. An entire series of alloys that do not require vacuum melting techniques and that generally provide good stress-rupture and impact properties was evolved.

The basic-alloy composition of 79 percent nickel, 8 percent molybdenum, 6 percent chromium, 6 percent aluminum, and 1 percent zirconium was modified by a series of element additions such as carbon, titanium, and boron, with the nickel content adjusted to account for the additives. Stress-rupture, impact, and swage tests were made with all the alloys.

The strongest composition (basic alloy plus 1.5 percent titanium plus 0.125 percent carbon) displayed 584- and 574-hour stress-rupture lives at 1800° F and 15,000 psi in the as-cast and homogenized conditions, respectively.

All the alloys investigated demonstrated good impact resistance. Several could not be broken in a low-capacity Izod impact tester and, on this basis, all compared favorably with several high-strength hightemperature alloys.

Swaging cracks were encountered with all the alloys. In several cases, however, these cracks were slight and could be detected only by zyglo examination. Some of these compositions may become amenable to hot working on further development.

On the basis of the properties indicated, it appears that several of the alloys evolved, particularly the 1.5 percent titanium plus 0.125 percent carbon basic-alloy modification, could be used for advancedtemperature turbine blades, as well as for possible space vehicle applications.

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INTRODUCTION

The continual demand for ever higher temperature materials having good load-carrying capacity, good oxidation resistance_ high strength-toweight ratio, and high impact resistance has been virtually insatiable insofar as jet engine applications are concerned. This has been particularly true with regard to turbine blades, where increases in operating temperatures of only i00° F can result in substantial engine thrust increases. Although the materials problems associated with space flight have not as yet been thoroughly assessed, the demand for materials of this type will probably be intensified when space vehicle applications are considered. Because of these known and anticipated requirements, an investigation was initiated at the NASALewis Research Center to explore the possibilities of extending the high-temperature properties of currently used materials with a view to turbine blade, as well as eventual space vehicle, applications.

Alloys currently employed for gas turbine blade applications are generally either nickel-base or cobalt-base compositions. The more refractory metals (molybdenum, tantalum, columbium, tungsten), although promising much higher "use-temperatures," are generally plagued by unsatisfactory oxidation resistance. As a consequence, it was considered most practical to investigate initially the possibility of achieving an advanced-temperature nickel-base alloy.

A survey of the literature indicated that extensive work already had been done by the various industrial producers, as well as by independent researchers such as Guy and Kinsey-Stewart ($refs. 1$ and 2), to provide new nickel-base alloys. Also, much work had been done to improve existing nickel-base alloys. For example_ investigations were madeto evaluate the effect of small additions of boron and zirconium that maybe picked up as crucible contaminants during melting (refs. 5 and 4). Additions of these elements in minute quantities were found gen_rally to improve rupture strength, and borom additions were found to reduce the tendency to notch brittleness. Thus, controlled additions of these materials became a powerful tool in improving nickel-base-alloy properties. As a result of these and other research efforts, maximum rupture properties of approximately 100 hours life at 15,000 psi and 1800 $^{\circ}$ F had been achieved with some nickel-base alloys (according to available published data) when the present investigation was initiated. The objective of this investigation was to determine whether significantly stronger nickel-base alloys could be developed for use at 1800⁰ F or above.

Preliminary studies indicated that a possibly productive area existed between the composition regions definel by Guy and Kinsey-Stewart. The latter investigators achieved strength and adequate oxidation resistance without the use of chromium by employing a large amount of molybdenum (21 to 22 percent) and a large amount of aluminum (7.76 to 8.36 percent)

as the major alloying constituents. Guy, on the other hand, utilized considerable chromium (12 to 15 percent) together with a much smaller quantity of molybdenum(5 to 6 percent) and a slightly smaller amount of aluminum (5.5 to 7 percent) as the major alloying constituents. Minor additions of columbium, iron, manganese, silicon, and boron are also included in Guy alloy; and minor additions of carbon, iron, and silicon are included in the Kinsey-Stewart alloy.

In making these preliminary studies, a literature survey was conducted, and trial melts of potential compositions were evaluated by stress-rupture tests. From this work a basic composition having fair stress-rupture properties, good oxidation-resistance properties and, more important, a potential for further improvement was developed. This composition (in wt. percent) was 6 percent chromium, 6 percent aluminum, 8 percent molybdenum, 1 percent zirconium, and the balance nickel.

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This report describes how the properties of the basic alloy were enhanced by additions of carbon, carbon plus titanium, titanium, and boron through such mechanismsas complex-carbide hardening, dispersion hardening through intermetallic compoundformation, and possibly solution hardening.

The alloys were evaluated on the basis of stress-to-rupture life, impact resistance, and formability. Short-time tensile test data at room temperature and at 1800^o F were also obtained for selected compositions. Hardness data were obtained for all the compositions investigated. Melts were made by high-frequency induction heating under an argon blanket. Investment casting techniques were employed in order to eliminate the need for extensive machining of test samples.

MATERIALS, APPARATUS, AND PROCEDURE

Alloys Investigated

The nominal compositions of the alloys considered in this investigation are listed in table I. The nomenclature used to designate the alloys is readily understood when the investigative procedure is considered. The basic alloy has a nominal composition of 79 percent nickel, 6 percent chromium, 6 percent aluminum, 8 percent molybdenum, and 1 percent zirconium. The variations from this composition include minor additions of carbon, titanium, and boron. In all cases these additions were accounted for by adjusting (i.e., subtracting from) the nickel content. The various compositions investigated are therefore referred to herein as the basic alloy plus the percent additives considered $(e.g., an alloy)$ with 1.5 percent titanium and 0.25 percent carbon is referred to as basic alloy + 1.5 Ti + 0.25 C). To provide an indication of the accuracy encountered in achieving the nominal compositions specified, chemical

analyses were made of heats chosen at random for virtually all the compositions investigated. These analyses were made by an independent chemical laboratory, and the results are shown in table II. Comparison of tables I and II indicates that the major loss in charging elements was that of aluminum, which, in view of its tendency to vaporize, might be expected.

Another element; zirconium, showsa slight degree of variation in weight percent in the chemical analysis of the alloys considered. This is probably due to the fact that a specific quantity of zirconium was not added as a melting constituent. Instead, zirconium was picked up from the stabilized zirconia crucibles used. Unavoidable variations in melting times would cause the melts to be exposed to the crucibles for varying time intervals. This in turn could result in differences in the amount of zirconium picked up. The average exposure time between melt and crucible was 20 minutes. Although the mechanism whereby the addition of zirconium improves the rupture properties of many alloys is not fully understood, the effect has been frequently observed. Recent investigations (ref. 5) into the mechanism of the beneficial effects of boron and zirconium additions to a complex nickel-base alloy indicate that boron and zirconium operate through two phenomena: They suppress the formation of noncoherent phases in the grain boundaries, and they retard the rate at which the γ' phase (intermetallic) is depleted from the matrix adjacent to the grain boundaries. The investigation of reference 5 was conducted with a titanium-aluminum-hardened _ickel-base alloy, and it may be that the mechanism established is applicable to other similarly hardened nickel-base alloys as well.

A fairly high degree of purity was maint{ined for the alloying elements added. The percent purities; as determined by the suppliers of the various materials used, were as follows:

Casting Techniques

Wax patterns. - Expendable wax patterns were made for the stressrupture bars, the swage bars, and the impact bars. These were prepared in precision dies and assembled as shown in *figure 1*. Three stressrupture bars, one swage bar, and two oversize impact bars with suitable gates and a riser formed one assembly. Of all the samples cast, only

the impact bars were oversize. This was done deliberately to permit machining the bars to exact tolerances so that the samples could all be gripped identically in the smoothvise jaws of the Izod tester. After being machined, the bars were cut in two sections to their proper length.

Mold preparation. - The wax pattern assembly was placed in an Inconel cylinder or flask open at each end, and a slurry of silica with a commercial binder was poured over it. After removing air from the investment in a vacuum chamber, the investment was allowed to settle for 48 hours. Excess moisture was poured off, and after another 24-hour drying period the invested flask was placed in a furnace to melt out the wax patterns. The furnace temperature was 200⁰ F when the invested flask was inserted. The flask was maintained at this temperature for 8 hours before a program of increasing temperature was initiated. The program consisted of increasing the temperature 200⁰ F in the first 16 hours and 75⁰ F per hour thereafter until an 1800° F temperature was attained. In this way, all wax traces were removed and the mold was cured. Several hours before casting, the mold temperature was dropped to 1600° F. All melts were poured into 1600° F molds, since this mold temperature was found to give satisfactory grain size.

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> Melting procedure. - A 50-kilowatt input high frequency $(10,000 \text{ cps}),$ water-cooled copper induction coil was used for melting. Melts were made in stabilized zirconia crucibles under an inert gas (argon) blanket. The crucible was surrounded by a graphite susceptor $1/2$ inch thick. This served a dual purpose of retaining heat along the entire crucible length as well as providing a deoxidizing atmosphere in the vicinity of the crucible.

In casting the basic composition, the crucible was first charged with nickel platelets and these were melted. Chromium platelets were added next; and after these melted, molybdenum chips were added. Approximately 5 minutes were allowed to permit the molybdenum to be satisfactorily dissolved. Aluminum slugs were added last, and the melt was poured within 50 seconds after the aluminum additions in order to permit retention of as much aluminum as possible. For the alloys whose compositions included boron, the boron was added last, together with the aluminum slugs, in the form of a compressed powder wrapped in an aluminum-foil case. The order of charge additions for alloys containing carbon and/or titanium was the same as for the basic alloy except that the compressed titanium and carbon powders (also wrapped in an aluminum-foil case) were completely surrounded and covered by the initial charge of nickel platelets. By submerging the titanium and carbon, it was possible to minimize the quantity lost. Zirconium was not added directly but was absorbed by pick up from the crucible as stated previously. The procedures described to make the alloying additions were evolved as a result of several attempts and were found to be the most satisfactory. The total weight of material per melt was approximately 760 grams.

Pouring temperature, as determined by optical pyrometer measurements, was 3150⁰ \pm 50⁰ F for all the compositions. All melts were top-poured into 1600° F molds without the inert gas coverage that had been maintained during the melting process, and the castings were permitted to cool slowly to room temperature (usually overnight) befcre removing the investment.

Inspection Procedures

All cast samples were vapor-blasted to provide a smooth surface before being inspected. Stress-rupture and swage bars were subjected to both radiographic and zyglo inspection prior to testing. The cast impact bars were first radiographed, then machined, and zyglo inspected after machining. Samples with significant flaws such as cracks or extensive porosity, as revealed by the inspection methods, were eliminated from further processing or testing.

Heat Treatment

All the compositions except the basic plus 0.4 percent boron modification were stress-rupture and impact tested in both the homogenized and the as-cast conditions. Although "homogenization" in the complete sense was not achieved at the relatively low temperatures employed, certainly a partial homogenization of the structures was achieved, and this term therefore will be used throughout this report. In addition, certain compositions were aged after the homogenization treatment, prior to rupture testing. A summary of the types of heat treatment employed for each of the compositions investigated is given in table III.

In most instances the homogenizing temperature chosen was the maximum value that could be attained without encountering melting at the grain boundaries. This was determined by microexamination of small samples, each heat-treated at a different temperature, in most cases 2000^o F . In a few instances rupture tests were made with samples homogenized at two different temperatures. These were cases where there was a question either as to whether grain boundary melting actually was occurring at the higher temperature or whether its presence ia minute quantities would adversely affect the test results. The final homogenizing time was 16 hours under an inert gas atmosphere (argon) in almost every case. In a few instances (see table) a 4-hour homogenization time was employed. In all cases air-cooling was employed upon remcval of the test samples from the heat treatment furnaces.

Alloy Property Determinations

Stress rupture and tensile tests. - Stress-rupture tests were run with all alloys at 1800⁰ F and 15,000 psi. This test condition forms a major basis of comparison of the alloys investigated. The stress level was chosen as being adequate for most high-temperature applications, since it exceeds turbine blade airfoil stresses in most current turbine engine designs. Additional stress-rupture tests were made with some of the alloys at 1600° , 1700° , and 1850° F. Other stress levels were also investigated in some instances. Virtually all alloys were run in the as-cast as well as the homogenized condition. Some were tested in a homogenized plus aged condition. Table IV summarizes all the stressrupture testing conditions.

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Tensile tests were made at room temperature and at 1800° F for both the basic alloy and what is perhaps its most promising modification, as selected on an over-all performance basis. These tests were run with ascast and homogenized samples. Two tests were run at each condition with both types of samples. The tensile test conditions are summarized in table V. Figure 2 illustrates the type of test bar used for both the stress-rupture and tensile tests. The conical heads served to eliminate stress concentrations that frequently cause premature specimen failure outside the test section. In this investigation no failures occurred at any point within the bars, except within the test section.

Impact tests. - Laboratory impact tests were performed for most of the alloys in the as-cast as well as the homogenized condition with a low-capacity Bell Telephone Laboratory Izod Impact Tester. This unit is described in reference 6. Tests were run with three, four, and in some cases five specimens of each alloy in both the as-cast and homogenized conditions. Impact test conditions are shown in table VI. The impact bars were 3/16 by 3/16 by $1\frac{1}{2}$ inches and were unnotched. Test bars were inserted in the grips of the tester to a depth of $1/2$ inch, and the point of impact of the pendulum was $1/8$ inch from the free end of the bar. Total capacity of the pendulum was 62.5 inch-pounds, and the striking velocity was 135 inches per second.

Workability. - Workability of alloys was determined by swaging. Ascast bars, approximately 0.530 inch in diameter, were fed through a halfinch swaging die. Attempts were made to swage all the alloys at room temperature as well as at elevated temperatures. The swaging conditions for the various alloys are listed in table VII. For hot swaging, the bars were heated in an induction furnace adjacent to the swager. A thermocouple was inserted into the furnace so as to contact the bar and thereby indicate when the desired temperature had been reached. The bar was then removed from the furnace with tongs, inserted into the swager for about I0 seconds, and quickly returned to the furnace. The rapid

heat dissipation to the cold dies required that such a procedure be repeated several times before the bar was swagedalong its entire length. Visual inspection for cracks was usually sufficient to determine lack of workability in the alloys. When no cracks were apparent, the bars were zyglo inspected.

Metallographic determinations. - All the alloys investigated were studied metallographically primarily to determine desirable heat-treating temperatures. Small samples of each alloy were examined metallographically after being subjected to various heat-treating temperatures in order to determine the limiting temperature at which traces of eutectic melting occurred. Photomicrographs were made of certain alloys and are presented herein.

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Hardness determinations. - Hardness data were obtained with a Rockwell hardness tester for all alloys in the a3-cast condition and for the basic alloy and its strongest modification in the homogenized condition. Hardness readings were also taken along longitudinal sections of fractured tensile bars to observe the degree of strain hardening, if any.

RESULTS

Stress-Rupture Dat_

Basic alloy. - A complete summary of all the stress-rupture data is given in table IV. The stress-rupture results are shown graphically in figures $3, 4$, and $5.$ The basic alloy (79 percent nickel, 8 percent molybdenum, 6 percent chromium, 6 percent allminum, and i percent zirconium) was stress-rupture tested in the as-cast condition as well as after several heat treatments (table IV). A 16 hour, 2100⁰ F homogenization treatment provided the best stress-rupture life at 1800° F and 15,000 psi. In the as-cast state, the basic alloy lid not demonstrate outstanding rupture properties at these test conditions; however, the homogenization treatment cited provided more than a threefold increase in life, from approximately 19 to 64 hours. Similarly, heat-treated samples of the basic alloy also demonstrated good rupture lives at lower test temperatures and a 15,000-psi load. At 1700⁰ F a rupture life greater than 900 hours was obtained, and at 1600° F the ripture life obtained exceeded 2900 hours. It is interesting to note that aging at 1600° F after homogenizing at 2100⁰ F increased the basic-alloy $.800⁰$ F, 15,000 psi rupture life to 89 hours. This suggests the possibility of further improvements with other heat treatments.

Basic alloy plus carbon additions. - F_{r.}gure 3 illustrates the effect of carbon additions on the 1800° F, 15,000 psi life of the basic alloy in both the as-cast and the homogenized conditions. Throughout this text, in cases where two homogenization treatments were attempted, the one giving maximum life (table IV) was plotted. Steadily improving life properties were obtained with increasing carbon additions for the as-cast condition.

The effect of the homogenizing treatments was to improve the life properties for each composition. Improvement in rupture life by homogenization occurred for both carbon additions, but there was not an appreciable difference in life between the compositions with 0.125 and 0.250 percent carbon in the homogenized condition. Both compositions exhibited approximately 130-hour life, a 100-percent improvement over the life of the homogenized basic alloy.

Basic alloy plus titanium additions. - The 1800° F, $15,000$ psi rupture life of the basic alloy was also improved by titanium additions, as shown in figure $4(a)$. Homogenization treatments substantially improved rupture life over the as-cast condition. 0ne-percent and two-percent titanium additions afforded no significant difference in the life of the homogenized samples, approximately 130 hours having been obtained for both alloys. If a smooth curve is drawn through these data points, as in the figure, it appears that the maximum life characteristics might be attained with an intermediate titanium content, say 1.5 percent. When the effect of carbon additions on the basic alloy (fig. 3) is considered, it is apparent that a similar amount of strengthening occurs with either carbon additions or titanium additions. In both cases the final results represent respectable rupture-life characteristics comparable to the better current high-temperature alloys.

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Basic alloy plus titanium and carbon additions. - Individually, carbon and titanium additives have been shown to benefit the basic-alloy rupture properties at 15,000 psi and 1800⁰ F. The effect of their combined addition to the basic alloy is shown in figure $4(b)$. Both 0.125 and 0.250 percent carbon, together with various percentages of titanium, were added to the basic alloy. In the as-cast condition the maximum life attained with one of these combinations was 384 hours. The 1.5 percent titanium and 0.125 percent carbon addition to the basic alloy provided this rather exceptional result. It should also be noted that results almost as good were obtained with the 0.25 percent carbon plus 2 percent titanium, and the 0.25 percent carbon plus 2.5 percent titanium additions - namely, 342 and 362 hours, respectively. Homogenization heat treatments again substantially improved rupture life over the as-cast condition except for the 0.25 percent carbon plus 2.5 percent titanium additions. The rupture life of the best composition (1.5 percent titanium plus 0.125 percent carbon addition to basic alloy) in the as-cast condition was improved further by as much as 51 percent by the homogenizing treatment. The outstanding fact apparent from the figure is, of course, the excellent rupture properties that can be achieved by combined carbon and titanium additions to the basic alloy.

Basic alloy plus boron additions. - The effect of boron additions on the 1800° F, 15,000 psi rupture life of the basic alloy is shown in figure 5. Figure $5(a)$ shows the results obtained with as-cast and homogenized samples, and figure $5(b)$ shows the results obtained from samples of these alloys after subjection to various homogenizing and aging treatments. A smooth curve was drawn through the best life data points. Only slight improvement in life over the basic alloy was realized for the ascast samples. Homogenization improved rupture life only for the O.Z percent boron addition. Beyond 0.2 percent ooron additions, rupture life was not improved by homogenization treatments.

Figure 5(b) presents ^a picture of steadily worsening life properties with increasing boron content. Two different homogenizing and aging treatments were attempted with each alloy. It was noted that increasing the boron content beyond 0.2 percent increased the tendency for eutectic melting. Consequently, lower homogenizing temperatures were necessary. Even these were not sufficiently low to eliminate melting entirely, however, and further temperature reductions would have resulted in no homogenization. Sometimes the adverse effects of melting can be compensated for by subsequent aging, and this was attempted. However, as shown in figure $5(b)$, the trend of decreasing life with increasing boron content was continued. These results indicate that boron additions to the basic alloy do not provide improvements in rupture life comparable to those obtained with carbon and titanium, and it is doubtful whether any aging treatment would materially change this picture.

Stress-rupture comparisons with current high-temperature alloys. - The previous figures show that rather high stress-rupture lives may be attained at 1800 ^O F and 15,000 psi with some of the compositions investigated. Figure $6(a)$ presents 1800⁰ F stress-rupture curves for several of these compositions, as well as for several other high-temperature alloys. It is immediately apparent that all the NASA compositions shown compare favorably with these high-temperature alloys. The best modification of the basic NASA alloy (on the basis of rupture life) has virtually the same 1800° F stress-rupture properties as vacuum-cast Udimet 700.

Figure $6(b)$ compares the basic NASA composition, as well as its strongest variation in the as-cast condition; for a constant 15_000 psi stress at several temperatures with two of tle better high-temperature alloys. Because of the extensive operating time required at temperatures below 1800⁰ F with a 15,000 psi stress, only the basic NASA alloy was rupture tested below 1800° F. The basic as-cast NASA alloy plus 1.5 percent titanium and 0.125 percent carbon agsin exceeds the life characteristics of all the other alloys shown except for cast Udimet 700, which it essentially duplicates. Although the stress-rupture data provide some indication that homogenization improves life, only the as-cast data are plotted for the NASA alloys in order to be conservative in the comparison. Additional investigations must be made to determine fully the effect of homogenization treatments on the life of these alloys. On the basis of these comparisons, the strongest NASA composition appears to represent a considerable advance over the majority of noncoated, oxidationresistant high-temperature alloys currently known.

Tensile Test Data

The tensile test data are summarized in table V. Yield strength (0.02 percent offset), percent elongation, and percent reduction in area are also listed. Values reported are averages of two tests conducted at each condition. The average difference between the two ultimate strength values obtained at each test condition was approximately 6000 psi. Tensile test data at room temperature and 1800° F (from preliminary data folder of the Kelsey-Hayes Co.), were available for two of the highest rupture strength high-temperature nickel-base alloys, wrought Udimet 600 and 700 (see fig. $6(a)$). These data are included in the table for comparison. There does not appear to be any significant difference between the as-cast and the homogenized condition for either NASA alloy. There is a definite difference between the general level of the results obtained with the basic composition and with the strongest alloy (1.5 percent titanium plus 0.125 percent carbon modification of basic alloy) investigated. The latter demonstrates higher ultimate tensile strengths at all test conditions. This difference is not too marked at room temperature, but it is significant at 1800° F, the modified alloy being approximately 40 percent stronger in the as-cast condition at the elevated temperature. Along with its higher strength properties, the modified alloy has significantly lower percent elongations and reductions in area than the basic alloy. Necking of the test bars, particularly those of the basic composition, was quite evident. It should also be noted that only negligible evidence of intergranular tears was apparent on microstructural examination of the failed tensile test bars. Consequently, the elongation values presented are reasonably indicative of the actual ductility.

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Comparison of the cast NASA alloys and the wrought commercial nickelbase alloys illustrates several interesting points. Both commercial alloys have appreciably greater room-temperature tensile strengths. At 1800° F, however, their ultimate tensile strengths are slightly lower than that of the modified NASA alloy. Both commercial alloys have considerably greater percentages of elongation and area reduction than the modified NASA alloy, although the basic NASA alloy demonstrates comparable values. The generally greater ductilities demonstrated by the commercial alloys are to be expected, since they are wrought products.

Impact Resistance

Impact resistance data for the alloys investigated herein as well as for several other high-temperature alloys are summarized in table VI. All the test results are listed. An average value is not given for each alloy because in many cases the samples could not be broken in the standard test. When the samples did not break, the impact resistance values are merely listed as being greater than 62.5 inch-pounds. For purposes

of comparison, impact data obtained for othe: high-temperature alloys with the same tester used in the investigations described in references 6 and 7 are also presented. It is apparent that all the alloys considered in the present investigation have good impact properties in the ascast condition. These properties are improved, or at least maintained, after heat treatment for 16 hours at 2000 \degree F in the basic alloy, the boron-modified alloy, and the simple carbon modification of the basic alloy. Titanium modifications greater than I percent and combined titanium plus carbon modifications of the basi: alloy show drastic declines in impact resistance after heat treatment.

Compared with the impact resistance of the high-temperature alloys shown in table VI, all the compositions investigated herein show up favorably, regardless of whether they were in the as-cast or homogenized condition. The lowest impact results obtained with any of the alloys investigated (homogenizedbasic alloy plus 2 percent titanium and 0.25 percent carbon) at room temperature are almost as high as the highest 1650° F impact results obtained with the other alloys shown. Onthe basis of these comparisons, the present allow series appears to have much to offer for applications requiring super alloy strengths as well as good impact resistance.

Workability

The results of swaging tests to determine the workability of all the compositions considered are shown in tab_e VII. Swaging was attempted at both room temperature and at leas_ one elevated temperature for all the alloys. The series of alloys with simple boron additions were swaged at several intermediate temperatures. What is immediately outstanding from the compilation of these da;a is the fact that none of the alloys could be satisfactorily swaged. 'There was a difference in the swageability of these alloys, however, a; evidenced by the fair and poor designations in the table. A fair designation indicates that there were few cracks and that usually these cracks were apparent only after zyglo inspection. A poor designation indicates that the cracks were immediately apparent and numerous.

Metallographic Studies

Photomicrographs of the basic alloy as $rel1$ as those of the 1.5 percent titanium plus 0.125 percent carbon m_dification are shown for the as-cast as well as the homogenized condition. Figure 7 provides photomicrographs of these alloys at two magn:.fications, X250 and X750, for the as-cast and homogenized conditions. This figure permits a general comparison of the two alloys. A more detailed study of the alloys may be made with figure 8, which presents the same alloys at a magnification of XISO0.

The basic alloy shows large quantities of eutectic-type structure in the grain boundaries. Upon heat treatment, part of this eutectic structure dissolves, and some of the matrix particles tend to agglomerate. The 1.5 percent titanium plus 0.125 percent carbon modification displays a somewhat different structure in the grain boundaries. Rather than appearing like a eutectic, this structure is more like a carbide network. Upon heat treatment, these grain boundary particles do not alter appreciably. The particles in the matrix, however, appear to become enlarged. The significance of these microstructures is discussed in a later section of the report.

Hardmess Data

Hardness data for all the alloys investigated are summarized in table VIII; average values are shown. Hardness data are presented for all the alloys in the as-cast condition and for the basic alloy and its strongest modification in the homogenized condition. No significant trend is apparent either with variations in composition from the basic alloy or for the heat treatments attempted. Rockwell "C" values were converted to the nearest whole numberfrom the experimentally obtained Rockwell "A" values by using a standard conversion table.

DISCUSSION OF RESULTS

0ver-all Evaluation of Compositions Investigated

Amyevaluation of the alloys investigated is dependent on their intended applications. In the present instance, assume these applications to be turbine blades for aircraft turbine engines, and various space vehicle uses. The requirements in the latter case have not as yet been completely defined. However, the high-speed high-temperature problems, such as reentry associated with space vehicles or missiles, and the high temperatures as well as thermal-shock problems associated with various parts of rocket powerplants will probably require the same type of properties, although considerably improved, as those required by turbine blades. With this background as a basis for evaluating the alloys investigated herein, good load-carrying capacity at high temperatures, good impact_ fatigue, and thermal shock resistance, as well as satisfactory oxidation resistance, becomemajor comparison criteria. All these properties are essential to a pronounced degree in turbine blade alloys and, as such, are likely requirements for the other applications noted.

in order to arrive at the best over-all composition uncovered by this investigation, the choice must be made from the results of stressrupture, impact, and workability tests, all of which were made during this investigation.

Consider first what is perhaps the most important property, stressrupture life. The maximum 1800° F, 15,000 psi rupture strength was demonstrated by a modification of the basic alloy consisting of 1.5 percent titanium plus 0.125 percent carbon $(fi_f. 4(b))$. In the as-cast condition, approximately equal life was attained with the 2 and 2.5 percent titanium plus 0.25 percent carbon modifications. In the homogenized condition, the 1.5 percent titanium plus 0.125 percent carbon modification of the basic alloy provided by far the best 1800° F, 15,000 psi rupture life.

A review of impact properties indicates that almost all the compositions tested have good impact resistance. The maximumimpact resistance recorded for the as-cast condition is more than 62.5 inch-pounds, and this occurs with several of the compositions examined. Others show an impact resistance only slightly under 62.5 inch-pounds. Homogenization treatments are beneficial in some instaaces and not in others, as previously noted. The lowest degree of impact resistance shown by virtually every alloy in this series would appear to be more than adequate for turbine blades as well as for considerably more severe applications. Such a conclusion can be drawn when the impact resistance of some highstrength high-temperature alloys (also shown in table VI) is considered. Turbine blades made from these alloys have been successfully engine operated without demonstrating undue brittleness (refs. 7 and 8), even though their room temperature impact resistance is one-fifth to onetenth that of the best impact resistant alloys of the present investigation.

On the basis of workability none of the alloys considered can claim remarkable properties. However, despite the fact that none of the alloys was successfully swaged, the variation in degree of swageability stands out. The presence of minor cracks in some of the alloys with simple titanium and simple carbon additions _o the basic composition, together with the fair results encountered with the basic alloy, would seem to indicate that with additional modifications several compositions show promise of becoming workable alloys. Further review of table VII shows that the boron additives and most of the combined titanium and carbon additives to the basic alloy are unfarorable from a swaging standpoint. In view of the preceding discussion, which showed the titanium plus carbon modification of the basic alloy to have the best stressrupture properties, this relative lack of workability may be an undesirable aspect, particularly if combined high rupture strength and workability are joint requirements for a given application. Of course, a final conclusion as to the exact degree of workability of any of these alloys can be made only by choosing the most favorable working temperature in each instance. Thus, for the present, it can only be concluded that all these compositions lend themselves primarily to casting techniques. For such applications as turbine blades, this is not necessarily a hindrance, since casting to a complex shape such as a turbine blade can be advantageous from a production time and cost standpoint.

Insofar as oxidation resistance is concerned, although no specific test to determine this property was run, it was apparent that no undue oxidation was encountered during the stress-rupture tests made with any of the alloys investigated. Thus, in a still-air atmosphere, all the alloys appear to be satisfactory at least up to 1800° F for the maximum lives demonstrated in each instance.

Summing up, on the basis of maximum rupture properties and good impact resistance, it must be concluded that the I.S percent titanium plus 0.125 percent carbon addition to the basic alloy is the most promising and has potential for advanced-temperature turbine blades and possible space vehicle applications. It also appears that slight variations in the titanium and carbon content with this alloy are well worth looking into, in view of the promising results attained with other titanium plus carbon modifications of the basic alloy.

Methods of Strengthening Basic Alloy

Strengthening by modification of existing types of intermetallic compounds. - The first method employed for increasing the basic-alloy rupture strength was to permit the formation of additional hard intermetallic compounds that tend to retard atom and dislocation movements. The commonly employed elements that produce both dispersion hardening and coherency strengthening of the matrix through intermetallic compound formation in high nickel alloys are aluminum and titanium. Since aluminum was included in the basic-alloy composition, nickel-aluminum intermetallic compounds presumably were already present and were contributing to the strength of the basic alloy. To further modify the nickel-aluminum intermetallic compounds, titanium additions were made. These a_ditions would permit the formation of a titanium-aluminum-nickel intermetallic compound (probably $Ni_{3}(A1, Ti)$) that was found to be responsible for the high strengths exhibited in a series of Ni-Cr-AI-Ti alloys by other investigators (ref. 9). Such titanium additions were also found to be beneficial in the present investigation. As shown in figure $4(a)$, approximately a lO0-percent increase in rupture life was realized.

The aluminum - titanium ratios considered in this investigation were approximately 6 to 1 and 3 to 1. Whether or not an optimum combination of these two elements was employed cannot be stated definitely from the limited data. However, there is no indication from figure $4(a)$ that any pronounced peaks in rupture life occur. A possible slight peak might be indicated at a 1.5 percent titanium content (4-to-I aluminumto-titanium ratio). Further investigation is required in order to establish the optimum aluminum-titanium ratio for this basic-alloy composition.

Carbide strengthening. - An attempt was also made to apply the principle of carbide strengthening, namely the provision of carbon and strong carbide-forming elements that tend to precipitate in the matrix as carbides, retardimg dislocatiom movements, in a manner similar to that of intermetallic compounds. This was dome by providing carbon as well as earbom plus titanium additions to the basic alloy. Since titanium is a very stable carbide former, titamium as well as carbon was added to the basic alloy with this purpose im mind. The improvements in rupture life of almost 600 percent shown in figure $4(b)$ should not, however, be arbitrarily ascribed to the more stable carbides alone. Rather, a combined strengthening effect due to the formation of $Ni3(A1,Ti)$ as well as complex carbides is probably responsible. By making such additions, it was intended that the carbon would go into solution and form additional dispersoids. The exact metallurgical mechanism that took place, however, is not known. Normal metallographic procedures do not show whether additional dispersoids (particularly carbides) are present in the matrix. It can be seen (fig. $8(c)$) that what appear to be carbides are present in the grain boundaries. These carbide particles c_n be strengthening. That they are stable is evidenced by their continued presence $(fig. 8(d))$ after heat treatment.

In view of the fact that a titanium plus carbon addition to the intermetallic-compound-hardened nickel-base alloy has a powerful strengthening effect, and since figure $4(b)$ indicates the possibility of achieving even better rupture life with other titanium plus aluminum plus carbon combinations, further investigation appears warranted to determine the maximum possible rupture properties. Of course, added strength at the expense of reduced impact resistance, which may occur with increasing titanium plus carbon additions (table VI), can curtail the applicability of such an alloy. The impact strengths shown for the higher titanium plus carbon additions to the basic alloy, however, are still rather high as compared with other superalloys, and some reduction probably could be tolerated without causing mdue brittleness.

Strengthening by boron additions. - An _ttempt was also made to strengthen the basic alloy by boron additions. Although the fundamental mechanism by which boron improves the rupture strengths of many alloys is not exactly understood, it has been shown to be effective in many cases (ref. 4); a possible mechanism has been advanced in reference 5 , as noted previously. The results of the present investigation suggest that the eutectic melting encountered with the NASA alloys as the boron content was increased has a deleterious effect on alloy rupture life. Certainly no pronounced trend of improved rupture properties such as was shown by the titanium or carbon addition; is apparent. This lack of consistency is perhaps not too surprising in view of the fact that the history of boron-containing alloys indicates that they are subject to erratic behavior. This behavior has been due, at least in part, to

the lack of understanding of the fundamental mechanism of boron strengthening (ref. 10). Since the 0.2 percent boron modification (when homogenized) showed improvement, it is possible that the peak in properties might be reached between 0 and 0.2 percent boron. Also, eutectic melting should have a less pronounced effect at these low boron contents. This is a possible area of further investigation for these alloys.

Metallographic Studies

The metallography performed sheds some light on the metallurgical processes involved. As noted previously, the 1.5 percent titanium plus 0.125 percent carbon modification shows a formation of carbides in the grain boundaries, as compared with a eutectic-type grain boundary structure for the basic alloy. This may account for the increased rupturelike properties of the modified alloy. Since the specimens examined were prepared by relatively conventional means, it was not possible to differentiate between matrix carbides and intermetallic compounds. Intermetallic compounds are believed to make up the vast preponderance of hard phases in the matrix. Although it is not visibly apparent, it is probable that some of the titanium and/or carbon may have strengthened the matrix as well. As to the stability of the basic alloy relative to the 1.5 percent titanium plus 0.125 percent carbon modification, one might compare the photomicrographs of figures $8(a)$ and (b) with those of $8(c)$ and (d). In the case of the modified alloy the grain boundaries did not change appreciably with heat treatment, whereas a marked change is apparent with the basic alloy. The matrix precipitates of the basic alloy agglomerate, although they remain finer than the precipitates of the 1.5 percent titanium plus 0.125 percent carbon modified alloy after heat treatment. The superior strength of the homogenized modified alloy relative to the strength of the homogenized basic alloy may be attributed in part to the more massive dispersoids present and possibly to dissolved titanium and/or carbon in the matrix.

Possibilities for Additional Evaluation and Development

The data presented indicate that a great deal of additional information could be obtained in order to present a complete picture of the alloys described herein. The general trends shown are in most cases sufficiently definitive, however, to delineate several approaches that may be employed in order to improve alloy properties further. Some of these possibilities may have been mentioned or implied previously. For the sake of clarity they are nevertheless included in this summary discussion.

One possibility for further improving rupture properties lies in increasing the percentages of some additive elements, such as titanium and carbon, to the basic alloy. Also, smaller incremental additions may be advisable if it is desired to pinpoint specific trends. Of course, the principle of alloying can also be extended to include additive elements other than those shown herein.

Possibly manyadditional approaches will suggest themselves to the reader interested in pursuing the development of these alloys, and the foregoing is intended only as an indication of the type of investigative procedure that may prove fruitful.

SUMMARY OF RESULTS

The following results were obtained from an investigation intended to provide an advanced-temperature nickel-base alloy:

1. A series of alloys that do not require vacuum melting techniques and that provide good stress rupture and impact properties was evolved. The basic-alloy composition was 79 percent nickel, 8 percent molybdenum, 6 percent chromium, 6 percent aluminum, and 1 percent zirconium. This composition was varied by systematic additions of carbon, titanium, and boron; and the nickel content was adjusted in each instance.

2. Most of the alloys evolved demonstrated rupture lives of i00 hours or more at 1800[°] F and 15,000 psi. The strongest composition (basic alloy plus 1.5 percent titanium and 0.125 percent carbon) displayed 384and 574-hour lives at 1800° F under this stress in the as-cast and homogenized conditions, respectively.

3. All the alloys demonstrated good impuct resistance. Several could not be broken in a low-capacity Izod inpact tester, and all compared favorably with several high-strength h:gh-temperature alloys.

4. All the alloys cracked upon swaging, although in several cases cracks were slight and could only be detected by zyglo examination, thus giving promise that on further development these compositions might become amenable to hot working.

Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio, January 16, 1959

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 $\frac{1}{2}$

 $\mathfrak z$ $\frac{9}{2}$

TABLE I. - NOMINAL COMPOSITIONS OF ALLOYS INVESTIGATED

TABLE II. COMPOSITIONS OF ALLOYS FROM RANDOMLY SELECTED HEATS

AS DETERMINED BY CHEMICAL ANALYSIS

[All run as cast except Basic + 0.4 B.]

 $C \beta 2 = \pi$

23

Ŷ,

a Data from Kelsey-Hayes Company preliminary data folder.

TABLE VI. - SUMMARY OF IMPACT DATA

 $\frac{a_{15}}{b_{\text{Data}}}\text{if }$ at 2000 $\frac{c}{x}$, air-cooled.

E-293

 $\begin{array}{c}\n1 \\
7 \\
1\n\end{array}$

25

TABLE VII. - SUMMARY OF SWAGING DATA

[As-cast condition; area reduction, 10 percent.]

 $\hat{\mathbf{v}}$

 \mathcal{A}^{\pm}

 $^{\text{a}}$ Rockwell "A" results are average of at least three tests.

bconverted from Rockwell "A".

 $\bar{\mathbf{r}}$

Figure 1. - Assembly of wax patterns for stress-rupture, swage, and impact bars.

Figure 2. - Drawing of tensile and stress-rupture bars employed. (All dimensions in inches.)

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Figure 3. - Effect of carbon additions on 1800° F life of basic NASA alloy at 15,000 psi stress.

$\Gamma \subset \Gamma \supset \mathcal{H}$

Figure 4. - Effect of titanium and titanium plus carbon additions on 1800° F life of basic NASA alloy at 15,000 psi stress.

Figure 5. - Effect of boron additions on 1800° F life of basic NASA alloy at 15,000 psi stress.

Time, hr

 1000

 $_{\text{LOO}}$

Figure 6. - Stress-rupture comparison of NASA alloys and representative commercial alloys.

1600

 $1500L$

 $10,000$

(a) Basic alloy, as-cast.

Figure 7. - Microstructures of basic alloy and 1.5 percent titanium, 0.125 percent carbon modification of basic alloy at low and inter-mediate magnifications.

Figure 7- - Continued. Microstructures of basic alloy and 1,5 percent titanium, 0.125 percent carbon modification of basi $\mathop{\mathtt{aut}}\nolimits$ at low and intermediate magnifications.

 $\bar{ }$ $\frac{1}{2}$

X750

(c) Basic alloy + 1.5 Ti + 0.125 C, as-cast.

Figure 7. - Continued. Microstructures of basic alloy and 1.5 percent titanium, 0.125 percent carbon modification of basic alloy at low and intermediate magnifications.

X750

(d) Basic alloy + 1.5 Ti + 0.125 C, heat-treated 16 hours at 2000[°] F.

Figure 7- - Concluded. Microstructures of basic alloy and $\verb|l.b percent titanium, 0.125 percent carbon modificat|$ of basic alloy at low and intermediate magnifications.

(b) Basic alloy, heat-treated 16 hours at 2000 $^{\circ}$ F.

Figure 8. - Microstructures of basic alloy and 1.5 percent titanium, 0.125 percent carbon modification of basic alloy at high magnification (X1500).

 $\label{eq:2.1} \frac{1}{\sqrt{2}}\int_{\mathbb{R}^3}\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2\frac{1}{\sqrt{2}}\left(\frac{1}{\sqrt{2}}\right)^2.$