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DEVELOPMENT OF DISPERSION-STRENGTHENED $Ni-Cr-ThO_2$ ALLOYS FOR THE SPACE SHUTTLE THERMAL PROTECTION SYSTEM

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SUMMARY

Dispersion-strengthened Ni-Cr-ThO_2 alloys are among the candidate materials being considered for use on the Space Shuttle Thermal Protection System (TPS). An extensive technology program is being sponsored by NASA to further develop these materials and to evaluate their potential for Shuttle use. This technology program covers development of improved sheet manufacturing processes, development of improved joining techniques, establishment of sheet formability criteria, establishment of design allowable properties, and determination of the effects of simulated re-entry exposure on properties. Prime emphasis has been placed on the Ni-20Cr-2ThO_2 alloy, TD-NiCr. An alternate alloy of similar composition, DS-NiCr, is included in the program.

An improved manufacturing process has been developed for TD-NiCr that provides sheet (45 x 90-cm, 18 x 36-in) of improved quality, better gage control, and reproducible properties. Manufacturing procedures for larger sheet sizes 60 x 150-cm (24 x 60-in) and foil have been developed. A standard manufacturing process has been developed for the alternate alloy, DS-NiCr, produced by pack-chromizing Ni-2ThO_2 sheet. Extension of forming and joining technology for TD-NiCr is in process. Formability criteria are

being established for basic sheet forming processes related to the manufacture of Shuttle TPS panels. They include brake forming, corrugation forming, joggling, dimpling, and beading. Joining processes applicable to TPS panels are being optimized with emphasis on establishment of joint efficiencies. Resistance spot welding (fusion and solid state), resistance seam welding, solid-state diffusion welding, and brazing are included in the joining programs. Development of improved manufacturing technology for TD-NiCr fasteners is also being accomplished. Mechanical and physical properties of TD-NiCr are being characterized to provide design-allowable data. This testing program is in process.

In the continuation of this technology program, major emphasis is centered on the development of an Al-modified Ni-Cr-ThO_2 alloy. The Al-modified alloys, containing 3 to 5 percent Al, form the more protective Al_2O_3 scale. This greatly enhances oxidation resistance under conditions of Shuttle re-entry, particularly the highest temperature of interest (1200°C, 2200°F), for use of dispersion-strengthened alloys. The Al-modified alloys are in the early stage of development. Both TD-NiCrAl and DS-NiCrAl alloys are included with prime emphasis on the TD-NiCrAl. A tentative composition of Ni-16Cr-3.5Al-2ThO_2 has been selected based on oxidation resistance and fabricability. Development of standard sheet manufacturing processes for the Al-modified alloys is in process.

INTRODUCTION

Dispersion-strengthened nickel-base alloys are currently being evaluated, along with other metallic materials, reusable surface insulation, and ablators for use in the hotter regions of the heat shields for the Space Shuttle (ref. 1). Among the metallic candidates, these alloys are attractive primarily because of their good high temperature strength. As shown in figure 1, the stress-rupture strengths of conventional superalloys (such as the nickel alloy Rene 41 and cobalt alloy HS-25) decrease quite rapidly with increasing temperature. So these alloys appear to be limited to heat shield regions which will see maximum temperatures of about 1000°C (1800°F). Above this temperature, the stronger refractory metal alloys could be used (for example, the columbium alloy Cb-752 or the tantalum alloy T-222). But these alloys rapidly oxidize in air and thus require protective coatings to resist oxidation under re-entry conditions. Because the reliability of these coatings is questionable for repeated use, it is desirable to minimize the use of coated refractory metals to only those areas where they are absolutely necessary.

The dispersion-strengthened alloys such as TD-NiCr (Ni-20Cr-2ThO_2) have adequate strength and oxidation resistance to be considered for use in an uncoated condition over a temperature range of about 980° to 1150°C (1800° to 2100°F), or possibly to 1200°C (2200°F). This temperature range is important because it could be associated with 30 percent or more of the heat shield area, depending upon the vehicle configuration and flight path. By using dispersion-strengthened alloys in this temperature range, the need for coated refractory metals, or nonmetallics, could be reduced to perhaps less than five percent of the heat shield area.

Although the dispersion-strengthened Ni-Cr alloys such as TD-NiCr offer considerable potential for Shuttle use, further development of these materials is needed to meet Shuttle requirements. Thus, NASA is conducting an extensive technology program to further develop the Ni-Cr-ThO_2 alloys and to evaluate their potential for Shuttle use.

The overall NASA technology program for the dispersion-strengthened Ni-Cr-ThO_2 alloys covers six major areas of development. They include:

1. The development of an improved sheet manufacturing process for TD-NiCr

2. The development of an alternate sheet manufacturing process (DS-NiCr)

3. The development of improved joining techniques

4. Establishment of sheet formability criteria

5. Establishment of design allowable properties

6. Determination of the effects of simulated re-entry exposure on properties.

Prime emphasis in this technology program has been placed on the Ni-20Cr-2ThO_2 alloy commercially termed "TD-NiCr." This alloy is produced by Fansteel, Incorporated, the only commercial producer of dispersion-strengthened metals in the United States. A smaller effort has been placed on the development of an alloy of similar composition, "DS-NiCr," produced by Sherritt-Gordon Mines, Ltd., Canada. More recently, aluminum-modified versions of these alloys (Ni-16 to 20Cr-3 to 5Al-2ThO_2) have shown improved oxidation resistance under simulated re-entry test conditions (refs. 1 and 2). So the technology program has also emphasized development of modified alloys (termed TD-NiCrAl and DS-NiCrAl).

These various technology programs are being conducted through a combination of in-house studies at several NASA Centers and contracted programs with various industrial organizations. The current status of these programs and future plans are summarized in the following sections.

DEVELOPMENT OF SHEET MANUFACTURING PROCESSES

Both TD-NiCr and DS-NiCr were in a state of "advanced development" at the start of our technology program. But considerably more development and sheet manufacturing technology existed for the manufacture of TD-NiCr sheet. Most of this technology was for 0.10 to 0.15-cm (0.040 to 0.060-in) gage sheet for aircraft engine components; whereas, sheet gages for Shuttle use range from foil to about 0.051-cm (0.020-in). Only TD-NiCr sheet was of commercial status. The development of DS-NiCr had just completed laboratory-scale feasibility studies. For both materials, considerable development was required to standardize the sheet manufacturing processes to yield a reproducible product with improved shape, finish, and gage control.

We are also pursuing the development of an advanced alloy with improved oxidation resistance to better meet the severe conditions of Shuttle re-entry. Emphasis has been placed on development of Al-modified Ni-Cr-ThO_2 alloys. These development studies and current results are described in the following sections.

TD-NiCr Development

Under NASA sponsorship (Contract NAS3-13490), Fansteel, Inc., has been conducting an extensive TD-NiCr development program. The major objectives of the sheet manufacturing portion of the program are to:

1. Develop a standard production process for the manufacture of sheet having uniform and reproducible properties and improved quality (flatness, gage control, and surface finish).

2. Develop the standard process for sheet sizes of 46 x 91 x 0.025 to 0.102-cm (18 x 36 x 0.010 to 0.040-in) and scale-up to sizes of 60 x 150 x 0.025 to 0.102-cm (24 x 60 x 0.010 to 0.040-in).

3. Develop a manufacturing process for thin foil (thicknesses of 0.008 to 0.013-cm, 0.003 to 0.005-in) in sheet sizes up to 60 x 150-cm (24 x 60-in).

4. Provide at least 680 Kg (1500-lbs) of sheet for other NASA Technology Programs.

The standard manufacturing process developed for the TD-NiCr sheet is outlined in figure 2. Powder manufacture is accomplished by a proprietary process. The powder is hydrostatically compacted in 45 kg (100 lb) units approximately 8 x 22 x 47-cm (3 x 8 x 18-in) and then sintered at 950°C (1750°F) in hydrogen with a dewpoint of -60°C (-70°F) or better. After sintering, the units are canned in mild steel and hot-roll consolidated at 1000°C (1850°F) to a thickness of 2.5-cm (1.0-in). At this step, the units are decanned, conditioned, and recanned. Rolling to intermediated plate (0.2-cm, 0.1-in) is done at 750°C (1400°F). After conditioning, the material is rolled to near-final gage at 750°C (1400°F) in steel cover sheets (0.16-cm, 0.06-in thick). The sheet is then recrystallized by heat treating at 1175°C (2150°F) for two hours. After recrystallization, the sheet is belt-sanded for final finishing (32 rms or better). For gages near 0.038-cm (0.010-in), the sheet is cold rolled (approximately 5 percent) to improve finish and flatness and then annealed for two hours at 1175°C (2150°F).

Product yield for this standard process is about 35 percent. This yield is at least twice that of prior practice which used either hot extrusion or forging as a means of consolidating the powder units (ref. 3). Also, the roll consolidation process is not as limited to scale-up as was the prior practice. Sheet manufactured by the standard process has better gage control, surface finish, and more reproducible properties.

Scale-up of the standard process for larger sheet sizes has been demonstrated. Sheet 60 x 150 x 0.025 to 0.102-cm (24 x 60 x 0.010 to 0.040-in) has been manufactured using 68 Kg (150-lb) units. Further development studies are underway at the present time to improve product reproducibility for the larger sheet sizes. Most of the continued development is in the warm rolling (750°C, 1400°F) portion of the process to improve handling of the larger sheet for closer control of the reduction per pass while maintaining proper shape.

Foil manufacturing processes also have been developed for TD-NiCr. Sheet produced by the standard process at 0.025-cm (0.010-in) thickness is cold tension rolled on a Sendzimir mill. High quality foil in gages of 0.008 to 0.013-cm (0.003 to 0.005-in) has been produced in sizes of 60 x 150-cm (24 x 60-in). The elevated temperature strength of the foil is less than that for warm-rolled material (e.g., about 83 vs. 110 MN/m^2, 12 vs. 16 Ksi, at 2000°F). But the foil has good bend ductility (<2t), flatness, and surface finish and is of interest for insulation packaging, where strength requirements are of less importance.

Over 900 Kg (2000-lb) of TD-NiCr sheet have been manufactured and furnished to NASA Centers and contractors for other phases of the Shuttle Technology Program such as property characterization tests and the forming and joining studies described herein.

DS-NiCr Development

Sherritt-Gordon Mines, Ltd., is developing an alternate process for the manufacture of Ni-20Cr-2ThO_2 sheet. This development program (under NASA Contract NAS3-14313) is not as extensive as the TD-NiCr technology program. The major objectives are to:

1. Develop a standard manufacturing process for producing DS-NiCr sheet in sizes of 60 x 122 x 0.013 to 0.075-cm (24 x 48 x 0.005 to 0.030-in).

2. Characterize mechanical properties of sheet manufactured by the standard process.

3. Provide at least 23 Kg (50-lb) of sheet to NASA for further evaluation.

The standard process that has been developed for the manufacture of DS-NiCr sheet is outlined in figure 3. The basic process consists of pack-chromizing DS-Ni (Ni-2ThO_2 sheet, a commercial product of Sherritt-Gordon Mines, Ltd.) to produce a nominal Ni-20Cr-2ThO_2 alloy. In the standard process, the DS-Ni sheet is pack-chromized at 1300°C (2350°F) in two 16-hour cycles at temperature. The chromizing pack consists of chromium powder (-325 mesh) mixed with about 5 percent of an inert oxide, such as yttria. Four sheets can be pack-chromized at the same time. After pack-chromizing, the sheets are homogenized by heat treating at 1300°C (2350°F) for 40 hours. Next, the sheets are stretcher leveled (total strain of 0.5 to 2.0 percent) and surface finished by wide-belt abrasive grinding. Final surface finish is better than 16 rms, and sheet flatness is better than 6 percent.

Chromium content of DS-NiCr sheet manufactured by the standard process is uniform throughout the sheet within $\pm$ 10 percent of nominal. Mechanical properties at elevated temperature (1100^{o}C, 2000^{o}F) are equivalent to the starting material. At ambient temperature, the DS-NiCr has higher yield and ultimate tensile strengths (about 200-280 MN/m^{2}, 30-40 Ksi) than DS-Ni due to solid-solution strengthening by the addition of Cr. A comparison of the typical mechanical properties of currently-available DS-Ni and DS-NiCr at 1100^{o}C (2000^{o}F) are given in Table I. Similar data for TD-NiCr are included.

As shown, DS-Ni and DS-NiCr have essentially the same strengths at 1100^{o}C (2000^{o}F). TD-NiCr has higher tensile strength and better stress-rupture properties. These data are for samples taken normal to the rolling direction. In the rolling direction, strength levels are about 10 to 20 percent higher for TD-NiCr and about 50 percent higher for DS-NiCr and DS-Ni. The greater anisotropy for the DS-alloys is related to the grain structure of the material evaluated to date--the grains have much greater elongation, length-to-width ratio, than TD-NiCr. We believe that this anisotropy can be reduced with proper changes in the manufacturing process for DS-Ni such that the mechanical properties of TD-NiCr and DS-NiCr would be comparable.

Continued studies on this program will include the manufacture of sheet for further evaluation and characterization of mechanical properties of either DS-NiCr or a DS-NiCrAl alloy. Development of a DS-NiCrAl alloy is described in the following section.

Al-Modified Alloy Development

With sufficient Al added to the Ni-Cr-ThO_2 alloys (about 3 to 4 percent), a protective Al_2O_3 scale is formed during high temperature exposure. The Al_2O_3 scale is much more protective than the Cr_2O_3 scale formed on Ni-Cr-ThO_2, particularly under Shuttle re-entry conditions (refs. 1 and 3) as discussed in the Re-Entry Effects section of this report. Thus, major emphasis is being placed on the development of a TD-NiCrAl alloy in the Fansteel program. This study includes optimization of the alloy composition and development of a standard manufacturing process.

Based on oxidation resistance and fabricability, the tentative composition selected is Ni-16Cr-3.5Al-2ThO_2. Development of a standard manufacturing process for this alloy is underway. The final process developed will probably be similar to that developed for TD-NiCr (fig. 2). But the rolling and recrystallization temperatures will probably be greatly different. For example, the experimental TD-NiCrAl alloys being manufactured at the present time are rolled at 1200°C (2200°F) to final gage and recrystallized at 1300°C (2400°F). The experimental TD-NiCrAl alloys produced to date are not quite as strong as TD-NiCr at elevated temperatures (e.g., about 20 percent lower tensile strength at 1100°C, 2000°F). But with improved processing conditions, we feel that the strength levels for the TD-NiCrAl alloys can be increased to approach those of TD-NiCr.

We are also in the process of developing an Al-modified alloy in the Sherritt-Gordon program. The DS-NiCrAl studies have just started. Preliminary results indicate that Cr and Al can be simultaneously introduced into the DS-Ni sheet using the basic pack-metallizing process illustrated in figure 3 for the manufacture of DS-NiCr sheet. Several alloy compositions are being evaluated, but the final composition selected is expected to be similar to that of TD-NiCrAl.

FORMING AND JOINING DEVELOPMENT

Forming TD-NiCr and DS-NiCr sheet into various configurations is not too difficult since these materials have good ductility at ambient temperature (e.g., 10 to 15 percent tensile elongation and 3t bend ductility). This ductility level is similar to that found in many superalloys currently in aircraft use. Thus, most cold-forming operations used for superalloy sheet structures should be applicable to these dispersion-strengthened materials. But actual formability criteria and limitations need to be established. An example of the fabricability of TD-NiCr is illustrated by the simulated heat-shield panels shown in figure 4.

Joining the dispersion-strengthened alloys presents a more difficult problem than forming. Conventional fusion-welding processes may be unacceptable for these materials. Fusion welding results in vaporization of the ThO_2 particles and alters the high-strength microstructure developed in the sheet manufacturing process. This results in weldments with about half the parent material's strength at elevated temperatures (refs. 4 and 5). Also, joint efficiencies for fusion weldments have been variable. Brazing TD-NiCr has been successfully accomplished using a nickel-base braze alloy termed TD-6 (ref. 4). The TD-6 alloy (Hastelloy-C with 4 wt. percent silicon) is a relatively high-temperature brazing alloy (1300°C, 2375°F) and is very reactive with TD-NiCr. Diffusion of silicon into TD-NiCr results in thoria agglomeration and subsequent loss of its strengthening effect. Excessive erosion is also a problem with the TD-6 alloy, particularly for the thin gage sheet required for Shuttle use. Thus, development of improved joining processes are required for Shuttle applications.

All of the present forming and joining technology studies are being conducted with TD-NiCr sheet since this material represents our major development effort. These studies are described in the following sections. Similar forming and joining technology studies are planned for the advanced Al-modified alloys.

Forming TD-NiCr Sheet

Development of forming technology for TD-NiCr sheet is being accomplished under NASA sponsorship (Contract NAS3-15567) by Convair Aerospace, Division of General Dynamics Corporation. The objective of this study is to establish actual and theoretical formability limits for five basic forming operations related to heat-shield panels. They are as follows:

1. Brake forming
2. Corrugation forming
3. Joggling
4. Dimpling
5. Beading

For each forming process, the most critical formability parameters required to evaluate the formability limits of TD-NiCr sheet are being determined. An example of critical formability parameters and the shape of the formability envelope are given in figure 5. For corrugation forming, the critical parameters are punch radius (R), corrugation angle (α), and material thickness (t). These parameters describe the formability envelope in the plot of R/t versus α. With forming conditions below the limit-curve, cracked parts result. Above the limit-curve, sound corrugations can be formed. Similar formability envelopes exist for the other forming processes as defined by their critical forming parameters.

Establishment of the theoretical formability limits for the five forming processes is being done using the forming predictability equations developed by Wood (ref. 6). Using this approach, the basic predictability equations relate the geometry of the formed part to the material properties. Convair has completed the theoretical analysis of the forming processes. Actual formability tests have just started. A comparison of actual and theoretical formability limits will be made to correlate any variations with forming variables (e.g., die design, lubricant, strain rate).

Since the mechanical properties of TD-NiCr are sensitive to structural change, the formed parts will be examined after heat treating (1200°C, 2200°F) to assess if forming strains for any of the processes evaluated cause structural changes in the TD-NiCr (e.g., recrystallization). Also, mechanical properties of samples selected from formed parts will be determined to assess any property degradation. Should this occur, the formability limits for that process will be adjusted accordingly to the level required to prevent property degradation.

In addition to forming TD-NiCr at ambient temperature as described above, warm forming (750°C, 1400°F) of unrecrystallized TD-NiCr is included in this study. Unrecrystallized TD-NiCr is standard TD-NiCr sheet which has not received the final recrystallization heat treatment. Warm forming of the unrecrystallized material is required since this material has nil ductility at ambient temperature. Formability limits for brake forming, corrugation forming, beading, and dimpling are being established in a manner similar to that described above for regular TD-NiCr. The prime reason for forming unrecrystallized TD-NiCr is related to the possible use of solid-state welding techniques to join TD-NiCr. Parent material properties can be achieved by solid-state welding TD-NiCr in the unrecrystallized condition as described in the following section.

At the completion of this study, the formability limits should be well established for TD-NiCr. These limits should be useful to manufacturers of hardware in selecting the proper forming parameters to assure the production of sound high-strength parts.

Joining TD-NiCr Sheet

Joining technology being developed for TD-NiCr includes fusion welding, solid-state welding, brazing, and fasteners. Optimization of resistance-spot-welding (both fusion and solid state) and resistance-seam-welding parameters (solid state), and the development of an improved brazing alloy are included in the Convair forming study. Establishment of joint efficiencies as well as process reproducibility are being emphasized for those joining processes. The development of fastener manufacturing technology is being accomplished in the Fansteel program through a subcontract to the Standard Pressed Steel Company. Both the Convair joining studies and the Standard Pressed Steel fastener development program are in the initial phase, and we have no significant results to report at this time.

Concurrently, joining studies are being conducted in-house at The Lewis Research Center. Most of this effort involves the development of solid-state-welding processes for TD-NiCr. A solid-state-welding technique has been developed that produces weldments as strong as the parent material both at ambient temperature and at $1100^{\circ}C$ ($2000^{\circ}F$) (ref. 7). Lap welds were made by vacuum-hot-pressing (200 MN/m^2, 30 Ksi) unrecrystallized (specially-processed material)

TD-NiCr sheet at about 700°C (1300°F) followed by a low-pressure (14 MN/m^2, 2 Ksi), high-temperature (1190°C, 2175°F) cycle. In this diffusion-welding process, the faying surfaces are brought into intimate contact in the first step. Recrystallization that occurs in the second step provides enhanced diffusion across the interface such that any evidence of a weld line is eliminated. The microstructure of this type of weldment is shown in figure 6(a). Good solid-state welds have been obtained also with regular (commercial) TD-NiCr, as shown in figure 6(b), but the weld line is still present. Strengths of both types of welds are equal to the parent material strength, as shown in the creep-rupture shear data of figure 7. Weldments produced with the unrecrystallized TD-NiCr were judged to be more desirable since failure always occurred in the parent material. Weldments produced with regular TD-NiCr always failed along the plane of the weld. Thus, we have included unrecrystallized TD-NiCr in the joining and forming technology studies.

Although it is unlikely that any of the other joining processes that involve fusion welding at brazing will match the strength of the solid-state weldments or elevated temperature, use of the other processes cannot be ruled out. For ease in manufacture and geometry restrictions, it may be advantageous to use fusion welding or brazing techniques in regions where 100 percent joint efficiencies are not required. But the establishment of the joint efficiencies for these processes and their reliability is required, and this represents a major portion of the joining technology study.

DESIGN ALLOWABLE PROPERTIES

Considerable mechanical and physical property data have been obtained by various organizations on TD-NiCr sheet manufactured during the past 8 years. A summary of most of the data has been compiled (ref. 4). These data were obtained during the early stages of the development of TD-NiCr and exhibit considerable scatter from heat to heat. This is probably due to changes made in the manufacturing process (and resulting microstructure) and variations in sheet gage. Thus, with the development of a standard manufacturing process for sheet gages applicable to Shuttle use, design-allowable properties have to be determined for this material. A large portion of this type of data is being obtained by Fansteel as a part of their manufacturing reproducibility studies. The additional data needed are being obtained in another program described in the following section. Establishment of design-allowable data for the advanced Al-modified alloy is planned and would be accomplished in a similar manner.

TD-NiCr Property Characterization

Property characterization tests for TD-NiCr are being conducted by Metcut Research Associates, Inc., under NASA sponsorship (Contract NAS3-15558). This program includes extensive testing of four heats of TD-NiCr sheet, 0.025 and 0.050-cm (0.010 and 0.20-in) gage, to establish both mechanical and physical properties from ambient temperature to 1300^{o}C (2400^{o}F). The mechanical properties being determined include tensile, creep, stress-rupture, bearing, compressive, shear, sharp-notch tensile, and fatigue strengths and the modulus of elasticity. Physical properties consist of thermal conductivity, thermal expansion, specific heat, and emissivity. The physical properties are being determined under subcontract by the Thermophysical Properties Research Center.

For the most important properties, the data are being treated on a statistical basis to define the 90 and 95 percent confidence levels. This property characterization program is in the early testing and data-accumulation phase. Only preliminary data are available at this time. These data indicate that the properties of TD-NiCr sheet have reasonably-small variations. For example, the 95 percent (-2σ) curve for the stress-rupture life at 875°C (1600°F) is only about 2 Ksi below the average (fig. 8). This is comparable to similar data obtained on the cobalt-base alloy HS-188 (ref. 8) also shown in figure 8.

This property characterization study will be completed in the latter part of this year. Sufficient property data with confidence levels should be available at that time to permit reliable use of the TD-NiCr alloy sheet in applications such as the heat shield of Space Shuttle vehicles.

RE-ENTRY EFFECTS

The severe Shuttle re-entry conditions can significantly alter material performance. For example, re-entry conditions impose three major conditions that affect the oxidation behavior of TD-NiCr. They are:

1. High temperature (870° to about 1200°C, 1600° to about 2200°F)

2. High velocity (in the range of Mach 8-12)

3. Low oxygen pressure (10 to 15 torr)

Some effects of these conditions on the performance of TD-NiCr and the recently-developed TD-NiCrAl alloy are described in the following sections.

Oxidation Behavior

TD-NiCr's reputation for excellent oxidation resistance at high temperature was based on the results of static furnace tests. Since the protective oxide scale that forms on TD-NiCr (Cr_2O_3) has an appreciable vapor pressure above about 1000°C (1850°F), a potential problem of enhanced oxidation under Shuttle re-entry conditions was recognized. This problem has been under evaluation at several NASA Centers using arc-jet tests to simulate re-entry conditions (refs. 2 and 9).

In the simulated re-entry tests, TD-NiCr does indeed oxidize more rapidly than in static furnace tests, as illustrated in figure 9. In low pressure (10 torr) static furnace tests at 1200°C (2200°F), the metal loss after fifty 1/2-hour cycles was only about 0.001-cm (0.0005-in). However, metal loss in the high-velocity, arc-jet tests was increased about three-fold. For the thin-gage Shuttle heat shields, this amount of metal loss might be excessive. Metallographic evaluation has shown the development of severe porosity in the TD-NiCr after arc-jet exposure. This is illustrated in figure 10(a). The porosity developed as a result of the loss of Cr due to the vaporization of Cr_2O_3. This degree of porosity and loss of Cr (about 50 percent near the surface) are expected to reduce mechanical properties.

The experimental TD-NiCrAl alloys have not shown this porosity after exposure to arc-jet conditions, as illustrated in figure 10(b). They form a protective Al_2O_3 scale that is not subject to vaporization under Shuttle re-entry conditions. The alloy illustrated in figure 10(b) contains about 0.2 yttrium. But other arc-jet tests of the TD-NiCrAl alloys without yttrium have given similar results. Metal loss of the TD-NiCrAl alloys in arc-jet tests at $1200^{\circ}C$ ($2200^{\circ}F$) has been less than half the metal loss for TD-NiCr.

Based on the test data obtained to date, it appears that the TD-NiCrAl alloys could be used at peak temperatures of $1200^{\circ}C$ ($2200^{\circ}F$). The peak use-temperature for TD-NiCr is probably 1100° to $1150^{\circ}C$ (2000° to $2100^{\circ}F$). Some property degradation is likely at these temperatures and would have to be accounted for in the heat shield designs. At peak temperatures of $1000^{\circ}C$ ($1800^{\circ}F$), TD-NiCr has performed satisfactorily in the arc-jet tests with minimal metal loss and porosity. But for overall performance, we feel that the TD-NiCrAl alloy is a better candidate material for Shuttle use since it forms a nonvolatile protective scale. Final selection will depend on the achievement of a high strength TD-NiCrAl alloy as discussed in the section on Al-Modified Alloy Development.

Additional arc-jet testing is underway at the Ames Research Center and their contractors to better define the use-temperature range of TD-NiCr and other candidate Shuttle materials. Studies of the effects of test variables are included to assist in defining use-temperature capability. For example, most of the tests conducted to date have used enthalpy values of about 6.7 MJ/Kg (3000 BTU/lb), whereas enthalpy values for the Shuttle are expected to be greater than 23 MJ/Kg (10,000 BTU/lb). Also, arc-jet tests have been conducted at about Mach 3 to 5. But for the Shuttle re-entry, Mach 8 to 12 is likely to be encountered. Thus, better re-entry simulation tests are required to determine the full capability of candidate materials such as TD-NiCr.

Effect on Properties

As noted in the preceding section, re-entry exposure is likely to degrade the mechanical properties of TD-NiCr particularly at the higher exposure temperatures (i.e., 1200°C, 2200°F). Initial tests conducted on small TD-NiCr samples (2.5 cm, 1-in diameter) after arc-jet exposure at 1150°C (2100°F) indicate 10 to 20 percent reduction in tensile strength at ambient temperature (unpublished data obtained from H. T. Sumsion and D. E. Wilson, NASA-Ames Research Center). Property tests of full-size specimens are required to check this behavior as well as the effects on high-temperature properties. Arc-jet exposure of larger samples, 10 x 10-cm (4 x 4-in), is now underway. Exposure conditions will cover the temperature range of 1000° to $1200^{\circ}C$ (1800° to $2200^{\circ}F$). Mechanical property tests after exposure will be conducted at ambient and elevated temperatures to better assess the effect of exposure on property degradation. Both TD-NiCr and TD-NiCrAl alloys are included. Results of this study should provide a first approximation of the effects of re-entry exposure on mechanical properties.

CONCLUDING REMARKS

Dispersion-strengthened Ni-Cr-ThO_2 alloys offer excellent potential for Shuttle use. Considerable progress has been made in the NASA technology programs to further develop these materials and to better define their capability for meeting Shuttle requirements. The manufacturing process for TD-NiCr sheet has been standardized to provide sheet of improved quality and reproducible properties. Manufacturing processes for larger sheet sizes and foil have been developed. A standard manufacturing process has been developed for an alternate alloy, DS-NiCr, produced by pack-chromizing Ni-2ThO_2 sheet.

Improvement of forming and joining technology for TD-NiCr is in process. Formability criteria are being established for basic sheet-forming processes related to the manufacture of Shuttle TPS panels. Joining processes applicable to TPS panels are being optimized with emphasis on establishing joint efficiencies for these processes. Mechanical and physical properties of TD-NiCr sheet are being characterized to provide design-allowable data. Results from these studies should provide the baseline data required to permit reliable use of TD-NiCr sheet in applications such as the Shuttle TPS.

Major emphasis in the continuation of this technology program is centered on the development of an Al-modified Ni-Cr-ThO_2 alloy. With additions of 3 to 5 percent Al, the alloys form the more protective Al_2O_3 scale. Based on the simulated Shuttle re-entry tests conducted to date, we are confident that the Al-modified alloys have adequate oxidation resistance for use at a peak temperature of 1200°C (2200°F). With proper control of the sheet manufacturing processes, we believe that the high-temperature strength levels of TD-NiCr can be achieved with the Al-modified alloys. Overall, there is a high probability of successfully developing the Al-modified alloys to the point of providing a material having better capability of meeting Shuttle TPS requirements in the temperature range of 980° to 1200°C (1800° to 2200°F).

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TABLE I. - REPRESENTATIVE MECHANICAL PROPERTIES OF

TD-NiCr, DS-NiCr, AND DS-Ni AT 1100° C (2000° F)[a]

Alloy	Yield strength, MN/m^2 (ksi)	Tensile strength, MN/m^2 (ksi)	Elongation, percent	Stress-rupture (100-hr life), MN/m^2 (ksi)
TD-NiCr	110 (16)	124 (18)	3	45 (6.5)
DS-NiCr	83 (12)	90 (13)	3	37 (5.3)
DS-Ni	76 (11)	90 (13)	3	37 (~5.3)[b]

[a]Normal to rolling direction.
[b]Tested in argon.

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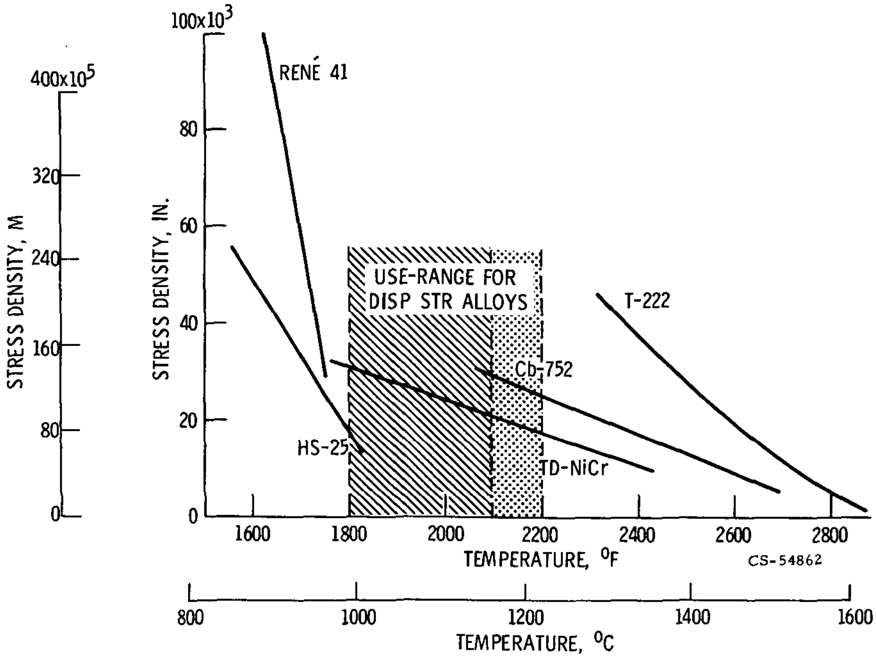

Figure 1. - Relative strengths of heat shield materials for a 100-hour stress-rupture life as a function of temperature.

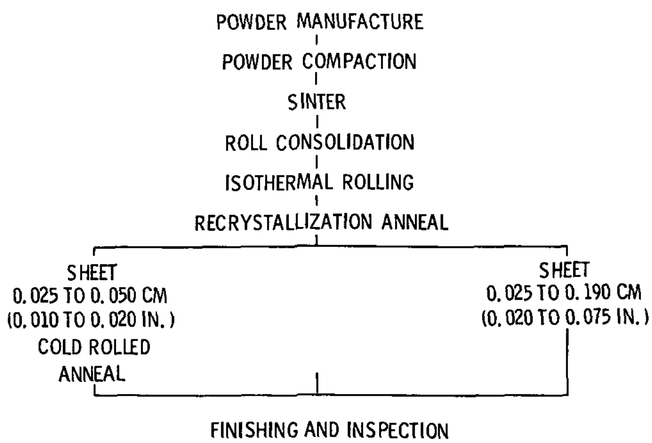

Figure 2. - Manufacturing process for TD-NiCr sheet.

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$Ni\text{-}2ThO_2$ SHEET (DS-Ni)

PACK CHROMIZE

HOMOGENIZE

STRETCH-LEVEL

SURFACE GRIND

INSPECTION

CS-62099

Figure 3. - Manufacturing process for DS-NiCr sheet.

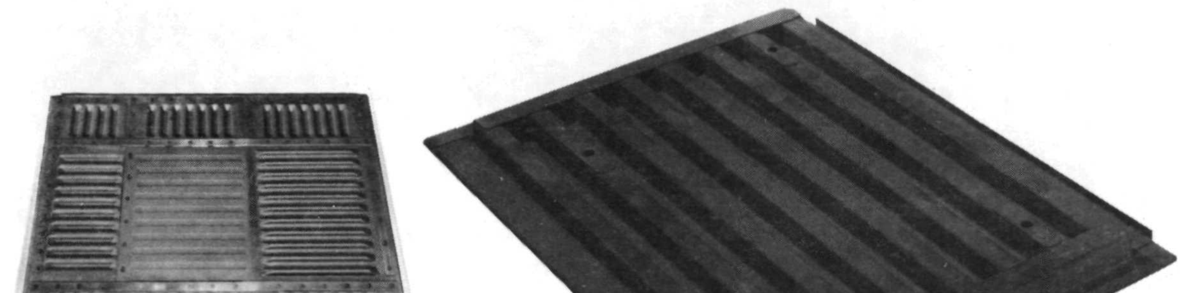

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Figure 4. - Experimental TPS panels fabricated from TD-NiCr sheet.

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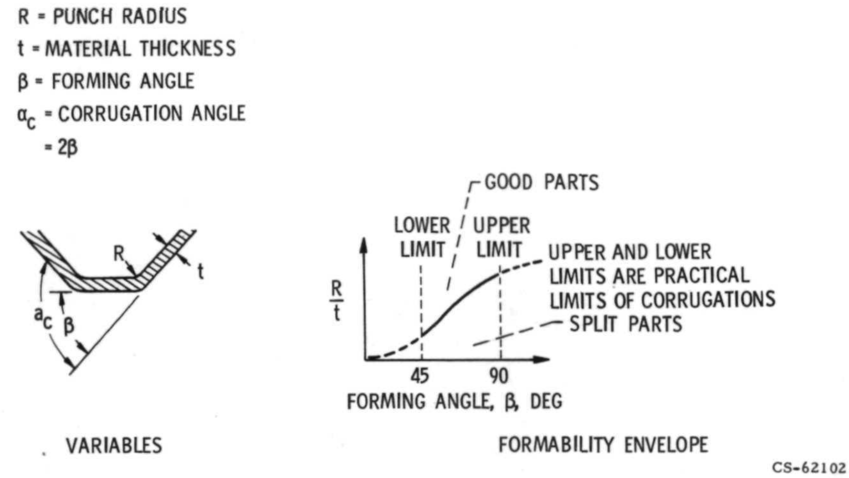

Figure 5. - Critical variables and formability envelope for corrugation forming process.

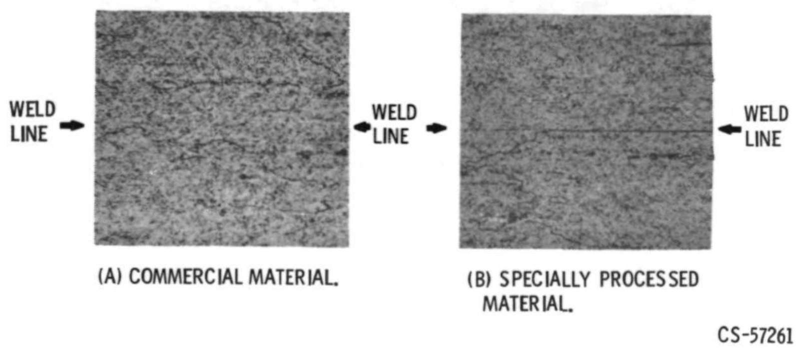

Figure 6. - Microstructures of solid state lap welds in TD-NiCr sheet. X500.

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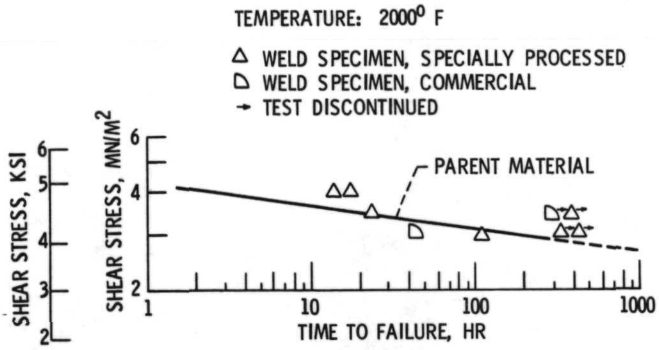

Figure 7. - Shear stress as function of time to rupture for parent and solid state (diffusion) welded lap joints in 1.6-millimeter (0.060-in.) TD-NiCr sheet at 1090° C (2000° F) in air. (All samples annealed at 1260° C (2300° F) for 1 hour prior to test.)

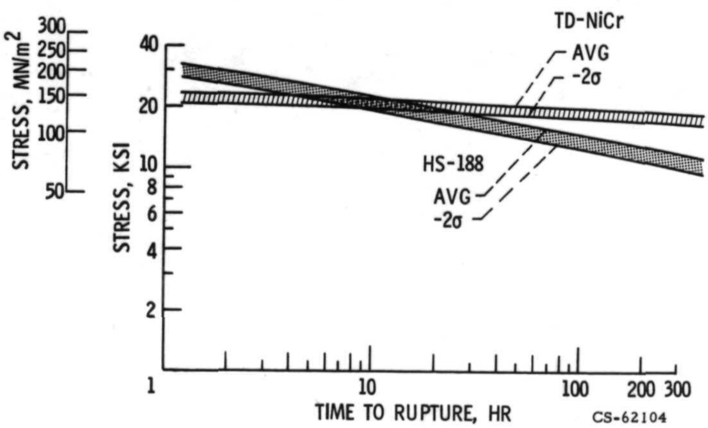

Figure 8. - Comparison of average and -2σ stress-rupture life for TD-NiCr and HS-188 at 875° C (1600° F).

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NO. OF 0.5 HOUR CYCLES: 50
AIR VELOCITY IN DYNAMIC TEST: MACH 5
PRESSURE:
STATIC - 10 TORR
DYNAMIC - 15 TORR

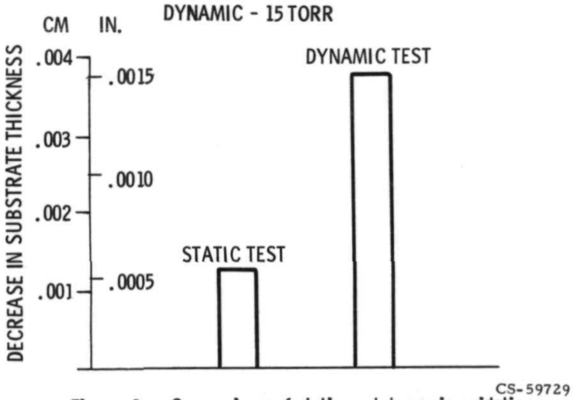
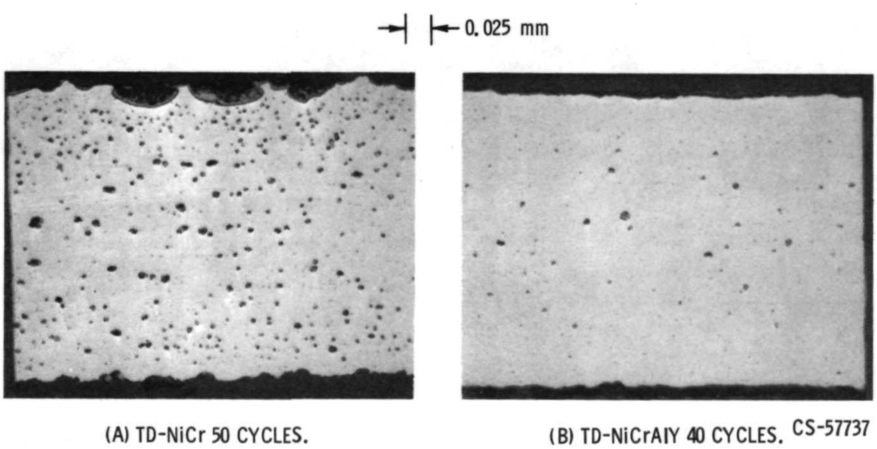


Figure 9. - Comparison of static and dynamic oxidation behavior of TD-NiCr sheet at 1200° C (2200° F).



(A) TD-NiCr 50 CYCLES.

(B) TD-NiCrAlY 40 CYCLES.

Figure 10. - Microstructures of TD-NiCr and TD-NiCrAlY after arc-jet exposure at 1200° C (2200° F). Tests conducted at a pressure of 15 torr and a velocity of Mach 5. Each cycle consisted of 30 minutes at temperature.