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LIQUID PHASE DENSIFICATION OF TITANIUM CARBIDE - NICKEL COMPOSITES

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(Ph.D. thesis)

November 1981

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LIQUID PHASE DENSIFICATION
OF TITANIUM CARBIDE - NICKEL COMPOSITES

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(Ph.D. thesis)

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This work was supported by the Director, Office of Basic Energy Sciences,
Division of Materials Sciences of the U. S. Department of Energy under
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ABSTRACT

Liquid phase densification of titanium carbide nickel composites was studied by high temperature scanning electron microscopy. The sintering kinetics were seen to be strongly dependent upon additions of free carbon to the system. Densification was progressively decreased with increasing carbon additions. These results are explained on the basis of changes in the eutectic reaction in the system, reduced solubility of titanium carbide in liquid phase, and decreased wetting of the solid by the liquid.

The influence of hydrogen heat treatment of particle compacts prior to sintering was also investigated. This processing resulted in the reduction of densification rates and elevated temperatures of liquid phase formation. Wetting experiments on hydrogen treated materials showed a time dependent contact angle. These results are discussed based on wetting theory and reactions predicted by the equilibrium ternary diagram.
I. INTRODUCTION

Metals and ceramics are often combined to form composites which have properties superior to those of either constituent. Examples of such composites are the families of materials commonly known as hard metals, cermets, or cemented carbides. Utilizing the metals of the iron group (Co, Ni, Fe) as ductile binders of the extremely hard carbides of the fourth to sixth group transition metals, materials of great toughness have been produced and extensively used as cutting tools and wear resistant parts.

Due to the very high melting temperatures of the transition metal carbides, the binder metals also serve the purpose of facilitating the densification of powder compacts by the process of liquid phase sintering.

Liquid phase sintering is the process by which, at elevated temperatures in the presence of a liquid phase, the surface free energy of a particulate system is reduced. This reduction in free energy is manifested in densification and changes in grain size and shape. The mechanical properties of cemented carbides are greatly influenced by the microstructures which develop during liquid phase sintering.\(^1,2\)

An understanding of the basic concepts of densification kinetics and microstructure evolution in these systems is, therefore, of practical interest.

Theoretical analyses of model systems have increased our understanding of liquid phase sintering. Three stages, differentiated by Kingery,\(^3\) are generally accepted as characteristic of liquid phase densification. These stages are:
1. Rearrangement stage - upon formation of a liquid phase, rapid densification occurs as liquid flow under surface forces causes rearrangement of solid particles.

2. Solution-Precipitation stage - with completion of the rearrangement process, increased solubility of particles at contact points results in a transfer of material to other surfaces resulting in a decrease in the center to center distance of particles and subsequent densification.

3. Coalescence stage - In systems where at equilibrium liquid does not separate solid grains a solid skeleton will form and densification and grain growth will proceed according to solid state mechanisms.

The kinetics of liquid phase sintering during these various stages have been modelled by a number of different investigators. These theoretical studies differ in their assumptions about specific mechanisms which predominate in each stage as well as the extent to which the different stages interact. The concepts common to these model analyses form the basis of our understanding of liquid phase densification.

In his kinetic analysis of the rearrangement stage, Kingery replaced interparticle capillary forces resulting from a liquid wetting a solid in a powder mass by an external pressure acting on the system as a whole. The resulting densification kinetics correspond to a viscous flow process following a relation:

\[ \frac{\Delta(L)}{L_0} = \frac{1}{3}\frac{\Delta(V)}{V_0}Kt \exp(1+y) \]  

where \( \frac{D(L)}{L_0} \) is the shrinkage of a particle compact equated to the volume change of the compact, \( \frac{D(V)}{V_0} \). The term, \( K \), is a temperature...
dependent constant, and the exponent of time is a number somewhat
greater than one (i.e. y is some small fraction). Kingery explained
this relationship as being a result of the increase in capillary forces
as pore size decreased with concurrent increase in resistance to
rearrangement as more efficient solid particle packing is attained.
The amount of densification that occurs by the rearrangement process
was noted by Kingery as being generally dependent upon the volume
fraction of liquid present.

In a more inclusive approach, Huppman related the interparticle
force between two solid particles separated by a liquid bridge to
rearrangement densification. This method offers the advantage of
including the influence of such parameters as the amount of liquid
phase and the wettability of the liquid on the solid.

The degree to which a liquid will wet a solid is determined by
conditions of thermodynamic equilibrium. Under chemical equilibrium
conditions, a liquid will wet a solid to a degree defined by Young's
equation:

$$\gamma_{sv} - \gamma_{sl} = \gamma_{lv} \cos \theta$$

where \(\gamma\) is the interfacial energy of the solid-vapor (sv),
solid-liquid (sl), and liquid-vapor (lv) and \(\theta\) is the angle measured
through the liquid phase as shown in Figure 1. Maximum wetting of the
solid would occur under equilibrium conditions when the reduction of
the surface energy of the solid-vapor interface by the liquid equaled
the liquid-vapor surface energy or, mathematically, when \(\theta\) is zero.

For two spheres connected by a liquid bridge the interparticle
force was shown by Heady and Cahn to be equal to:

$$F = (2\pi \gamma_{lv} \cos \phi) - \pi r^2 \Delta P$$
and consists of a surface tension term acting at the wetting perimeter $2\pi r$ and a term arising from capillary pressure $\Delta P$. $\gamma_{lv}$ is the surface free energy of the liquid vapor interface, and $r$ and $\phi$ are defined in Figure 2. Depending upon the relative volumes of the solid particles and liquid, wetting angle $\theta$, and interparticle distance $D$, the interparticle force will be either attractive (positive force) or repulsive (negative force). The model experiments of Huppman on planar arrays of tungsten spheres and oxidized tungsten spheres in a copper melt, systems exhibiting mutual insolubility, confirmed the validity of numerical solutions of equation (3). Only an approximate relationship relating shrinkage to these forces is possible, however, due to the interlocking of solid particles which impedes rearrangement shrinkage. Huppmann offers the relationship:

$$\frac{(\Delta L)/L_0}{\text{rearrangement}} = K(F-F_0)$$

with the interpretation of a rearrangement shrinkage dependent upon the interparticle force, $F$, exceeding an intrinsic force, $F_0$, required to breakdown solid particle bridges. The dependence of rearrangement shrinkage on homogeneity of particle mixing, packing density, and particle shape expected from the influence of these properties on solid bridge formation has been shown in both real and model systems although quantitative relationships cannot be given. While Kingery does not consider its importance in the kinetics of initial rearrangement densification, Huppmann, as well as Whalen and Humenik, point out that solution processes and particle rearrangement are concurrent in most systems. It has been observed experimentally in the liquid phase sintering of real powder compacts that the initial shrinkage is much greater in systems in which the solid is highly soluble in the liquid.
This can be explained by increased rearrangement as small particles
dissolve and particle bridges collapse due to increased solubility at
contact points. The dissolution of components can also lead to a
reduction in the effective wetting angle of equation (3) leading to
higher effective interparticle forces. Aksay et. al.\textsuperscript{9} have
established the effect of interfacial solution chemical reactions on
wetting mechanics under chemical nonequilibrium conditions. They state
that mass transfer across an interface results in a transient decrease
in the corresponding interfacial free energy by an amount equal to the
free energy change of the effective chemical reaction per area at that
interface. Recent studies by Pask and Tomsia\textsuperscript{10} and Sharps et.
al.\textsuperscript{11} have refined this theory and have shown that mass transfer of a
component of the liquid phase into the solid is required for spreading
to occur. This reduction in the effective solid-liquid interfacial
energy and thus in wetting angle $\theta$ would lead to larger interparticle
forces according to equation (3) promoting rearrangement.

With the assumption that the liquid completely separates solid
grains and that rearrangement and solution precipitation stages occur
independently, Kingery derived the time dependence of shrinkage of
spherical and prismatic grains as a function of the rate controlling
mass transport process. Table I summarizes the results of this
analysis.
<table>
<thead>
<tr>
<th>Time dependence</th>
<th>Rate Controlling Mechanism</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A(L)/L_0 \sim t^{1/2}$</td>
<td>Phase boundary (solution) controlled reaction of spherical particles</td>
</tr>
<tr>
<td>$A(L)/L_0 \sim t^{1/3}$</td>
<td>Diffusion controlled reaction of spherical particles.</td>
</tr>
<tr>
<td>$A(L)/L_0 \sim t^{1/3}$</td>
<td>Phase boundary (solution) controlled reaction of prismatic particles</td>
</tr>
<tr>
<td>$A(L)/L_0 \sim t^{1/5}$</td>
<td>Diffusion controlled reaction of prismatic particles.</td>
</tr>
</tbody>
</table>

Gressinger, Fishmeister, and Lukas\textsuperscript{6} modelled the second stage of liquid phase sintering in more detail. These investigators based their derivations on the force acting on the grain-grain contact area between two spherical particles. This force,\[ F = 2\pi r \gamma_{lv} - \pi (r^2 - x^2) \gamma_{lv}(1/e+1/r) + 2\pi \gamma_{sl} \sin \psi/2 \] includes components from the surface tension of the wetting phase, the capillary pressure arising from the liquid vapor interface, and a third term arising from the interfacial tension $\gamma_{sl}$ at the grain boundary.
between the solid particles (Fig. 3). It is a more general form of Eq. (3) active in the rearrangement stage with inclusion of the influence of the formation of solid-solid interface. Numerical methods were used to relate this force to the chemical potential gradient leading to mass transport along the grain boundary. The shrinkage kinetics which they predict are only a slight modification of Kingery's equations when liquid penetrates the grain boundary.

The simple geometry of such models limits their application to real systems. In addition, the experimental difficulties of isolating rearrangement shrinkage from solution-precipitation shrinkage make comparison of experimental shrinkage measurements to model kinetic equations an unconvincing argument for identification of densification mechanisms. Prill et. al. have shown that the exponent of time for solution-precipitation densification is critically dependent upon the amount of shrinkage attributed to rearrangement processes. The consequence of assuming exact transition points between different stages has been a range of mechanism identifying exponents and resulting disagreement of rate controlling processes even when interpreting identical data.

The final stage of liquid phase sintering is one of particle growth. This stage normally leads to little densification but is of interest due to the importance of grain size on mechanical properties.

The growth of solid particles in a liquid matrix is normally considered to occur by solution precipitation processes. From this point of view experimental results have been discussed on the basis of the theoretical kinetic equations derived by Lifshitz and Slyozov, and Wagner for the Ostwald ripening of second phase solid particles.
in a liquid matrix. In general the particle growth rate can be described by the formula,

\[ r^n - r_0^n = Kt \]

where \( r \) is mean radius at time \( t \), \( r_0 \) is the initial particle mean radius, \( K \) is a temperature-dependent constant and \( n \) is an exponent of value 3 for diffusion controlled growth and of value 2 for solution controlled growth. Theoretical derivation was based on spherical particles, noncontiguity of the solid phase, and no interaction of diffusion zones around particles. These conditions are not fulfilled in real liquid phase sintering systems. Exner et. al.\textsuperscript{14} have pointed out that the exponent in the grain size time relationship is not a valid criterion for determining the rate controlling mechanism growth. The steady state size distribution of particles growing in a liquid phase predicted by theory is a more accurate technique according to these investigators. In real systems with small volume fractions of liquid phase the applicability of model equations is unknown, however. Determining the mechanism of particle growth is complicated by the process of grain coalescence. Coalescence is the process by which contiguous grains grow by solid state mechanisms. The relative values of the solid-solid and liquid-solid surface free energies determine the possibility of coalescence. The dihedral angle seen in Fig. 4 is a measure of the degree of intergranular penetration of a liquid under equilibrium conditions. The value of the dihedral angle, \( \phi \), is determined by the magnitude of grain boundary and liquid-solid interfacial energies (\( \gamma_{ss} \) and \( \gamma_{ls} \) respectively) according to,

\[ 2\gamma_{ls} \cos(\phi/2) = \gamma_{ss}. \]
Coalescence appears to lead to rapid grain growth in some systems although the influence of anisometric surface energies and contiguity effects are not known.

The three stages of liquid phase densification have been theoretically analyzed based on model systems. These analyses have predicted the influence of interparticle forces acting on a solid in a liquid matrix on shrinkage kinetics in both the rearrangement and solution-precipitation stages of liquid phase densification. The application of model equations to experimental shrinkage values of real powder systems is restricted by more complicated geometries, nonuniform particle packing, irregular particle shape, particle size distributions and the mutual interaction of rearrangement and solution-precipitation processes. Although kinetic equations cannot be given for densification in these systems, it is expected that the factors which determine the interparticle forces; solubility of components, relative volume fractions of solid and liquid, relative interfacial energies of solid, liquid and vapor and resulting wetting and grain boundary formation will be those factors which determine the empirical kinetics of liquid phase sintering. The liquid-phase densification of titanium carbide - nickel composites was studied with specific attention to the effects of processing on these factors.

The titanium carbide - nickel system offers advantages in use to the more traditional cemented carbide composite, tungsten carbide - cobalt. These advantages include oxidation resistance at high temperature, higher strength to weight ratio, and higher hardness. In addition recent studies in this field revealed increased tool life in the machining of steel.
II. EXPERIMENTAL

1. High-Temperature Microscopy

Original modifications of a commerical specimen heating device for the JSM-U3 model JEOL scanning electron microscope have been previously described. These design changes centered around the construction of a more reliable heater, increased radiation shielding and modification of the thermal electron suppression grid. With these modifications the temperature capability was increased from 1100 C to 1600 C. Operation at high temperatures was possible for periods up to five hours. Continuous improvements in the specimen heating stage have enabled the direct observation of materials at temperatures of 1750 C over a 24-hour period.

The improved heater consists of a nominal 0.265 in. I.D. by 0.405 in. O.D. Lucalox tube diamond ground to an O.D. of 0.388 in. The outside diameter of this tube was threaded by diamond grinding to give 0.025 in. deep grooves with 26 threads per inch. The tube was cut to give sections 0.35 in. in length. A second tube of 99% alumina with dimensions 0.415 in. I.D. by 0.5 in. O.D. was of similar length. At approximate positions a slot and notches 0.10 in. wide were cut in the tube walls with a diamond saw. The smaller tube was mounted on a post and wound with six turns of 0.015 in. thoriated tungsten wire as shown in Fig. 5A. The tungsten wire was bent, the larger tube slipped over the assembly and fine 99% alumina tubes were slipped over the wire leads for insulation (Fig. 5B). The completed heating element is shown in Fig. 5C surrounded by molybdenum radiation shielding.
Figure 6 shows the assembled specimen stage carrier. In Fig. 6A the heating element and surrounding radiation shielding are seen on the stainless steel base plate of the specimen stage carrier. The electrical connections of the heating element extend to the sides of the carrier where they are pinched by copper pieces attached to alumina side plates. Within the heating element, a tungsten foil can be seen. A W-5%Re/W-26%Re thermocouple spot welded to the underside of this foil provides temperature measurement. The foil and thermocouple are supported within the heating element by an alumina stand machined to reduce heat loss. The insulated thermocouple wires extend to the right end of the specimen carrier where they are looped around screws supported by an alumina endplate. Fig. 6B shows the fully assembled specimen stage carrier with top molybdenum radiation shielding and top coverplate fastened by screws in the corners of the carrier.

In Fig. 7A the specimen stage carrier is observed with electrical connections made on the inside of the SEM stage. The thermocouple wires are located to the lower left on the specimen stage. Connections are made to posts wound with .010" W-5%Re and W-26%Re wire which lead to external connections. Likewise the copper heater connections on the specimen stage make pressure contact with copper plates within the main stage. These copper plates are wired to a power supply connector.

Since the thermocouple is positioned at a distance from the sample the thermocouple reading was calibrated to give the true specimen temperature. The main stage is placed in the vacuum chamber shown in Figure 8. A calibrated optical pyrometer is focused on the sample through holes in the top radiation shielding. The stage was calibrated for different heating rates by recording both the power drawn by the
heating element and the optical pyrometer reading for every 20 degree incremental increase in the recorders indicator. Figure 9 shows the heater power input versus the thermocouple reading.

The temperature calibration curve for the constant heating rate used in this study (8 degrees/min.) is shown in Figure 10. The temperature of the sample is always higher than the thermocouple reading. This is most likely a result of the proximity of the thermocouple to the water cooled base plate. The difference in temperatures is not constant. At 900C, for example, the sample is 55 degrees higher than the thermocouple reading. At 1350C the difference in temperatures is 75 degrees. The accuracy of the optical readings were determined by comparison with the observable melting of high-purity metals within the scanning electron microscope. The melting temperatures of silver, copper, and nickel were repeatably within ± 5 degrees of the expected values. Hereafter, all temperatures referred to will be the calibrated values.

2. Materials and Sample Preparation

The titanium carbide and nickel powders used in this study were obtained from CERAC INC. and Cotronics, respectively. Received as a -325 mesh material, the titanium carbide was specified 99.5% pure. Carbon analyses indicated a carbon content of 18.8 - 19.0 weight percent corresponding to a composition of TiC_{0.92} to TiC_{0.94}. Norton and Lewis\textsuperscript{17} gave TiC_{0.95} as the upper boundary of the extremely wide composition range of single phase TiC\textsubscript{x} (Fig. 11). Determination of the lattice constant of this material by precision x-ray analysis gave a lattice constant of the cubic unit cell of a = 4.329 Å. This value corresponds to a composition of TiC_{0.95} although the lattice parameter
is an imprecise method of determining composition in this material because of its sensitivity to oxygen contamination.

The nickel was specified 99.9% pure and was received as material size separated below 10 microns. To ensure control over the particle size of the starting materials, both the titanium carbide and the nickel were individually size separated using an Aminco Particle Size Analyzer. Particle size separation is achieved by directing a jet of air through an agitated powder sample within a settling chamber. A specified, calibrated flow rate can be determined to carry away particles below a certain size which are then collected. A flow rate was chosen for each material to separate particles with a largest size of 10 microns. Figure 12 shows the powders thus obtained. The titanium carbide is prismatic with particle size ranging from submicron to largest particles of approximately 10 microns (Fig. 12A). The nickel is of narrower size distribution consisting of rough multigranular particles predominantly between 2 to 8 microns as measured in the micrographs (Fig. 12B).

Samples for sintering studies were prepared by careful weighing and mixing of powders to give compositions ranging from TiC - 10 weight percent Ni to TiC - 30 weight percent Ni. The materials were mixed in a reagent grade isopropyl alcohol in polyethylene bottles placed in a SWECO vibratory mill for a minimum of 24 hours. The powders were allowed to dry in air at 75 C in evaporation dishes. Based on the separate theoretical densities of the constituents, a theoretical density of each composition was calculated. An amount of each composition was carefully weighed to give a 60% dense sample of size 0.48 cm. in diameter by 0.155 cm. in height. Samples of this size were
pressed in a hardened tool steel die with uniaxial pressure. No binders were added during the pressing operation.

To study the effects of additional carbon on densification, colloidal graphite was added to separate batches of the above compositions. The colloidal graphite was added as the commercial product Aquadag which is a suspension of graphite in isopropyl alchol. Various amounts of Aquadag were weighed in beakers and added to the TiC - Ni - isopropyl mixtures before mixing in the SWECO mill. Processing then followed the steps listed above.

A number of samples of the varying compositions were heat treated in hydrogen before the sintering runs in the vacuum of the scanning electron microscope. The hydrogen treatment consisted of heating and cooling samples in flowing, ultrapure, dry hydrogen. The maximum temperatures of these heat treatments ranged between 500 and 800°C. Isothermal holds at the maximum varied between 0.5 and 2 hours.

The reproducibility and accuracy of these processes in producing homogeneous samples was determined by the analysis of pressed samples for Ni content. The results of these analyses are shown below.

**TABLE II**

<table>
<thead>
<tr>
<th>Nominal Composition</th>
<th>Ni content (random sampling)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC - 10wt.% Ni</td>
<td>9.96%, 10.04%, 10.30%</td>
</tr>
<tr>
<td>TiC - 20wt.% Ni</td>
<td>19.78%, 20.26%</td>
</tr>
<tr>
<td>TiC - 30wt.% Ni</td>
<td>29.47%, 29.80%</td>
</tr>
</tbody>
</table>

* Wet chemical analyses performed by American Spectrographic
The carbon content for the TiC - 10wt.% Ni samples was also determined for the various processing treatments. The results of these carbon analyses are shown in Table III. Analyses were performed with a LECO WR-12 carbon determinator. Carbon content of a sample is determined by this instrument through its complete oxidation in flowing oxygen at 1650°C. The CO and CO₂ combustion products are measured by thermal conductivity techniques. The accuracy of the instrument is specified at ±0.002wt.% carbon for carbon content up to 5 wt%. For the higher carbon content of the titanium carbide samples the accuracy will be reduced. Analysis of 100% TiC samples yielded results reproducible to ±0.1 Wt.% carbon.

**TABLE III**

<table>
<thead>
<tr>
<th>Composition</th>
<th>Pre-sintering heat treatment</th>
<th>Carbon Wt.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC-10wt.%Ni</td>
<td>none</td>
<td>17.3 %</td>
</tr>
<tr>
<td>TiC-10wt.%Ni+C</td>
<td>none</td>
<td>17.6 %</td>
</tr>
<tr>
<td>TiC-10wt.%Ni+C</td>
<td>none</td>
<td>18.4 %</td>
</tr>
<tr>
<td>TiC-10wt.%Ni+C</td>
<td>none</td>
<td>19.8 %</td>
</tr>
<tr>
<td>TiC-10wt.%Ni</td>
<td>1/2 hour at 500°C in hydrogen</td>
<td>17.2 %</td>
</tr>
<tr>
<td>TiC-10wt.%Ni</td>
<td>1 hour at 600°C in hydrogen</td>
<td>17.1 %</td>
</tr>
<tr>
<td>TiC-10wt.%Ni</td>
<td>1/2 hour at 800°C in hydrogen</td>
<td>16.7 %</td>
</tr>
<tr>
<td>TiC-10wt.%Ni</td>
<td>1 hour at 800°C in hydrogen</td>
<td>16.5 %</td>
</tr>
</tbody>
</table>

*Carbon analysis is performed by Anamet Labs, Berkeley, Ca.*
3. **Shrinkage Measurements**

To study the linear dimensional changes of the powder compact during liquid phase densification, alumina microspheres (44 microns dia.) were placed on the sample surface to serve as reference points. Shrinkage could be measured then by the change in distance between microspheres. The spheres were randomly distributed by tapping a small spatula on which they were held over the sample. To ensure their stability, the spheres were lightly pressed on the surface. The sample was placed upon a sapphire substrate within the high temperature stage heating element. The high temperature stage was then inserted within the main stage of the SEM and the system was evacuated to a vacuum of $10^{-5}$ torr. The sample was rapidly heated to $700^\circ$C and held at this temperature for 1/2 hour. The sample was brought into focus at this temperature and an area was selected which at low magnification (70-100x) provided the best distribution of spheres for a statistical sampling of shrinkage.

A constant heating rate of 8 degrees/min. from $700^\circ$C was used in shrinkage runs. At every 20 degree interval at this rate of heating a polaroid camera was used to record the image of the SEM TV scanning image. As densification proceeded the sample was kept in focus by raising the specimen stage. This maintained a constant working distance and eliminated changes in magnification accompanying focal adjustments. The ability of the SEM to rapidly increase and decrease magnification enabled an accurate determination of the temperature of formation of the liquid phase in the fine powder at high magnification while not interfering with the recording of the low magnification dimensional changes. The formation of the liquid phase was evidenced from flow of liquid around solid particles.
The ability to clearly view geometric changes during sintering is limited by a one micron resolution in the high terperature SEM. This is a result of the difficulty in detecting secondary electrons emitted from the cavity of the heating element. Emission of thermal electrons which can mask the secondary electron image also reduces resolving capability.

Microstructural changes evident at high temperatures in the presence of a liquid phase in the TiC-Ni system are shown in Figure 13. In Fig. 13A and 13B an alumina sphere on a TiC-Ni compact is seen at 700°C. It is possible to identify some large prismatic grains as TiC. The smaller grains of Ni and smaller grains of TiC cannot be differentiated, however. In Fig. 13C and Fig. 13D the same area is observed at a temperature of 1300°C. In these micrographs, liquid phase is present. Some of the large prismatic carbide grains can still be identified surrounded by a liquid phase.

To obtain shrinkage measurements, the negative of each polaroid photograph was projected using a photographic enlarger. From these enlarged images, the distances between the reference microspheres were measured. At least five measurements at each temperature were made to obtain a statistical average of shrinkage. The measurements at 700°C were used as initial values of interparticle distance, Lo, and shrinkage was calculated at each temperature from

\[
\frac{1}{n} \sum (L - Lo) / Lo
\]

where L is the interparticle distance and n is the number of measurements at each temperature. Examples of the pictures taken from the TV scanning image during high temperature shrinkage runs are seen in Figure 14.
4. Wetting Studies

The wettability of nickel-titanium carbide systems were determined for correlation to measured shrinkage kinetics of powder compacts. The wetting properties were measured by the sessile drop technique in vacuo. The experimental apparatus consisted of a horizontal graphite resistance furnace within a vacuum chamber. Ports sealed with fused silica windows allowed optical access to the samples. A diffusion pump provided a vacuum of $3 \times 10^{-6}$ torr. The oxygen partial pressure of this system is very low due to the graphite heating element. An oxygen partial pressure of $\sim 10^{-18}$ torr was calculated from thermodynamic data on carbon oxidation and the assumption that the measured pressured resulted from carbon monoxide.

Titanium carbide discs, hot pressed to 94% theoretical density were obtained from CERAC INC. This material was of 99.5% purity. The 3/4" diameter by 1/8" thick samples were polished with a series of diamond pastes (6, 1, 0.25 microns) on Syntron vibratory polishers. After polishing the samples were ultrasonically cleaned in acetone and isopropyl alcohol. From the x-ray diffraction pattern of the polished samples a lattice parameter of $a=4.328\text{Å}$ was determined.

Cotronics nickel powder was pressed into cylindrical samples which were fractured to give small pieces of powder compact. These pieces were placed upon the polished TiC substrates and heated in the vacuum of the graphite furnace until a liquid phase formed. The wetting angle, $\theta$, was measured by a reticuled telescope focused on the nickel sample along the plane of the TiC substrate.

To study the effect of excess carbon on the wetting properties of Ni on TiC, graphite in isopropyl alcohol (the commercial product
Aquadag) was mixed with the nickel powder in isopropyl alcohol, dried and pressed into powder compacts following the process used to prepare samples for sintering runs. These unfired samples were broken, placed upon the polished TiC discs, heated in vacuum and sessile drop measured.

Both polished TiC samples and Ni powder compacts were heat treated in high purity, dry, flowing hydrogen at 800°C for two hours prior to sessile drop experiments to determine the effects of these process conditions on wettability.
III. RESULTS AND DISCUSSION

1. High Temperature Microscopy Densification

The results of the high temperature scanning electron microscope densification experiments are presented in Figures 15-23. Percent shrinkage is plotted beginning at $1100^\circ C$ because shrinkage was not significant for samples at lower temperatures. The shrinkage data have been plotted as the average value of a minimum of two experimental runs for each composition. As a minimum of 5 shrinkage measurements were made at each temperature, these curves represent an average shrinkage value of at least 10 measurements. The deviation from these average shrinkage profiles is typically greatest immediately after the formation of a liquid phase with standard deviations of $\pm 1\%$ measured. Such spread in values is a result of both the real inhomogeneity of the particle compacts and the accuracy of the high temperature stage in temperature measurement.

In Figure 15 the shrinkage characteristics of TiC-Ni compacts of varying Ni concentration are compared. At a constant rate of heating of 8 degrees/minute, the densification of compositions with 10, 20 and 30 wt% Ni commences at approximately $1220^\circ C$. Upon formation of a liquid phase at $1290^\circ C$, as observed at high magnification, the rate of densification rapidly increased in the traditional rearrangement region of liquid phase sintering. As expected, the greater the volume of liquid phase the greater is the initial densification. On constant heating to $1360^\circ C$, linear shrinkages of approximately 9% for TiC-10wt%Ni, 11% for TiC-20wt%Ni, and 14% for TiC-30wt%Ni are measured.
In Figures 16, 17 and 18, the influence of carbon added as graphite on shrinkage results in these systems is presented. The most detailed evaluation was performed on the TiC-10wt% Ni system. In Fig. 16 the shrinkage profile for the composition with 17.3 wt.% carbon content represents those samples to which no carbon was added. It can be seen in this figure that, depending on the amount present, free carbon in TiC-Ni compacts can greatly inhibit densification. With a slight increase in carbon (0.3 wt.%), little change in shrinkage is seen. As carbon content increases to 18.4 wt.%, however, a significant change in sintering behavior is observed with shrinkage becoming apparent at lower temperature but leading to reduced shrinkage rate upon formation of liquid phase which was again observed at an approximate temperature of 1290°C. The inhibition to densification is more pronounced when the carbon content is increased to 19.8 wt.% or an approximate addition of 2.5 wt.% carbon. Formation of a liquid phase was not observed in these powder samples during sintering runs to 1360°C. The shrinkage curve for this composition reflects this observation with small amounts of shrinkage measured and no increase in densification rate characteristic of systems in which a liquid forms and wets the solid.

Comparison of the microstructures of sectioned and polished particle compacts of 17.3 wt.% C and 19.8 wt.% C titanium carbide-nickel composites after constant heating to 1360°C with a one hour isothermal hold at this temperature can be seen in Fig., 19. Final shrinkages for the low and high carbon samples after isothermal hold were 13% and 9%, respectively. The increased densification of the 17.3 wt.% sample can be seen to be associated with a more homogeneous
distribution of liquid around grains. Such a liquid distribution, associated with a liquid wetting the solid particles, is more conducive to densification than isolated liquid areas due to the increased liquid-solid surface area and greater redistribution of solid through the liquid phase.

Liquid phase in the high carbon content sample apparently formed even though it was not observed in the high temperature SEM. This will be explained by changes in the eutectic reaction in this system and by results of wetting experiments.

The results in the TiC-10wt%Ni compositions were supported by shrinkage measurements in TiC-20wt%Ni and TiC-30wt%Ni compacts to which carbon was added. As seen in Fig. 17, the addition of approximately 0.9 wt.% carbon to TiC-20 wt.% Ni powder compacts results in a decrease in the temperature at which shrinkage becomes evident and a decrease in densification rate after liquid phase forms. In Fig. 18, the shrinkage of a TiC-30 wt.% Ni composition is compared with a composition with a high carbon content. Initial shrinkage is not significantly affected by the increased carbon content but densification is greatly reduced after formation of a liquid phase which was observed at approximately 1290°C. At 1360°C, the high carbon samples showed an average shrinkage of ~7% compared with ~14% for samples with no additional carbon.

The sintering kinetics of TiC-Ni composites in the high temperature SEM were seen to be sensitive not only to additions of free carbon but also to pre-sintering heat treatments in hydrogen. The shrinkage of TiC-10wt%Ni compacts as a function of hydrogen treatment is seen in Fig. 20. Again, the samples of 17.3 wt.% carbon have not
been heated in hydrogen and contain no additional carbon. A progressive decrease in carbon content with increased temperature and time of hydrogen treatment was determined. With increased temperature and/or time of hydrogen treatment the shrinkage of these power compacts is also progressively inhibited. This decreased sinterability becomes measurable after H2 treatment at 600°C for 1 hour. At a constant heating rate of 8 degrees/min. samples treated in hydrogen showed an average shrinkage of 〜7.5% compared with an average value of 9.0% for those samples untreated. When the temperature of hydrogen treatment is increased to 800°C, the densification of TiC-10wt%Ni is further reduced. Powder compacts which were exposed to dry, flowing hydrogen at this temperature for 1/2 hour formed liquid phases at 1290°C. It was not possible to distinguish any difference in liquid wettability in the SEM. Little densification resulted, however, from this liquid phase formation. At the constant rate of heating to 1360°C an average shrinkage for such samples was 2.5%. When the length of time of H2 treatment at 800°C was increased to 1 hour, liquid phase densification did not occur up to 1355. Liquid was not observed until the temperature reached 1355°C and in qualitative observation did not appear to flow as readily in the compact.

The effects of hydrogen heat treatments on densification of TiC-10wt%Ni powder compacts were also observed in composites which contained 20 and 30 wt.% nickel. In Fig. 21 the influence of hydrogen treatment of TiC-20wt.% Ni at 800°C for 1/2 hour on sintering kinetics is seen. As in the composition containing 10wt% nickel, densification is greatly reduced. Liquid phase was observed at 〜1290°C in both treated and untreated materials. In the
densification of TiC-30wt%Ni samples (Fig. 22), similar behavior is seen for identical heat treatment with a reduced rate of shrinkage observed on formation of a liquid at 1290°C as compared with untreated samples. TiC-30wt% Ni samples treated in H2 at 800°C for 2 hours and sintered in vacuum in the SEM showed no liquid phase until a temperature of 1355°C similar to the TiC-10wt% Ni sample treated for 1 hour at 800°C. At 1355°C, at high magnification in the SEM, the nickel particles appeared to be undergoing abrupt changes in appearance as would happen with formation of liquid phase. Spreading of a liquid around solid particles was not observed, however.

In Fig. 23, micrographs of fractured TiC-30wt% Ni compacts are seen. A comparison is made in this figure of the microstructures of particle compacts with and without hydrogen treatment after heating to 1360°C. In Figures 23 A, C, and E the TiC-30 weight percent sample which underwent hydrogen heat treatment before sintering is seen at various magnifications. The light contrast areas were identified by x-ray fluorescence as nickel. The granular shape of these Ni regions supports the observation in the high temperature SEM that liquid did not form and wet the carbide grains. In comparison, Figs. 23 B, D, and F are identical magnifications of the TiC-30 weight percent nickel compact that underwent no hydrogen treatment. X-ray fluorescence revealed Ni at the intergranular regions of TiC grains.

In compositions containing both 20 and 30 wt.% nickel, initial shrinkage at low temperatures before a liquid has formed is increased by heat treatment in hydrogen at 800 C for 1/2 hour. This increased shrinkage is not observed for the longer heat treatments at this temperature. Table IV summarizes some of the observations made in the high temperature SEM sintering of TiC-Ni composites.
In comparing the shrinkage curves for the various compacts and processing conditions of this study a common feature is the significant change in shrinkage rate under the constant heating rate conditions at a temperature of approximately 1340°C. This change could be the manifestation of the reduced contribution of rearrangement processes to densification of the compacts and the onset of coalescence phenomena. Another interesting observation is the increased densification of samples with additional carbon and hydrogen heat treatment at temperatures below the observed liquid phase formation temperature. Similar results were observed by Exner et al. with increased pre-liquid phase sintering of tungsten carbide cobalt particle compacts in a system with increased carbon content. Explanation was related to the removal of oxygen from the carbide structure as measured by an increase in the CO content of the system during sintering. The presence of oxygen contamination in the carbide of this study was determined by Auger analysis and will be discussed further in a later section. It appears that the increased initial sintering of higher carbon and hydrogen treated material is related to the reduction of this oxycarbide surface.
<table>
<thead>
<tr>
<th>PROCESSING CONDITION</th>
<th>OBSERVATIONS</th>
</tr>
</thead>
<tbody>
<tr>
<td>No additional carbon</td>
<td>Liquid phase forms at $\sim 1290^\circ C$</td>
</tr>
<tr>
<td>No hydrogen treatment</td>
<td>Highest densification rates upon formation of liquid phase</td>
</tr>
<tr>
<td>Additional carbon added</td>
<td>Liquid phase forms at $\sim 1290^\circ C$ for all compositions except</td>
</tr>
<tr>
<td>to systems</td>
<td>TiC-10wt%Ni with $\sim 2.34$wt% C added no liquid phase observed for this</td>
</tr>
<tr>
<td></td>
<td>composition</td>
</tr>
<tr>
<td></td>
<td>Slightly increased amounts of shrinkage at low temperatures</td>
</tr>
<tr>
<td>Pre-sintering</td>
<td>Increase time and/or temperature of treatment decrease sinterability of</td>
</tr>
<tr>
<td>heat treatment in</td>
<td>Liquid phase forms $\sim 1290^\circ C$ for all compositions except those</td>
</tr>
<tr>
<td>hydrogen</td>
<td>treated at $800^\circ C$ for 1 hour or more. Liquid observed at $\sim 1355^\circ C$</td>
</tr>
</tbody>
</table>
2. **Densification and Ternary Equilibrium Compositions**

The liquid phase densification of titanium carbide-nickel composites is strongly dependent upon the composition of the system. This can be better understood through an examination of the nickel-titanium-carbon ternary. A tentative $870^\circ C$ isothermal section of this system, as determined by Stover and Wulff is presented in Fig. 24. The ternary is complicated by the number of intermetallics in the Ni-Ti system and the wide composition range of the carbide (49 at.% carbon to 37 at.% carbon at $870^\circ C$). In Fig. 24, alpha is the low temperature titanium phase, beta the higher temperature titanium polymorph, gamma the nickel rich solution, and delta the carbide. Each of the Ni-Ti intermetallics is in equilibrium with a delta carbide phase. The sensitivity of equilibrium compositions to slight changes in the carbon content of the carbide which results is apparent. The solubility of nickel in titanium carbide is not known to have been determined. Stover and Wulff measured a slight increase in lattice parameter of carbide melted in the presence of nickel although they state the solubility is not above a fraction of an atomic percent. A quasi-binary eutectic in a vertical plane intersecting the Ni-Ti binary at ~9 at.% Ti and the Ti-C binary at ~48 at.% C exists between carbon rich delta and gamma. Ternary eutectics occur on either side with TiNi or with carbon. Stover and Wulff determined the solidus in various phase regions and these are given in Table V. Estimated projections of the liquidus between eutectic points (dot - dash lines) and boundaries between three phase fields containing liquid on the invariant plane (dash lines) are indicated in Fig. 24 for the gamma-delta-carbon ternary, and gamma-delta-TiNi$_3$ ternary.
The carbon analysis of the titanium carbide of this study indicated an approximate composition of TiC_{.93} or 48 at.% C (18.9 wt.%). An ideal TiC_{.93}-10 wt.% Ni composition would have a carbon content of 17.0 wt.%. The analysis of the carbon content of the TiC-10 wt.% Ni particle samples of the densification studies indicated a slightly higher carbon content 17.3 wt.% (Table III) which may result from the combined influences of accuracy of carbon analysis, sample...
preparation, and contamination during blending in plastic bottles. Points 1-4 in Fig. 25 are the compositions of TiC-10wt%Ni (17.3 wt% C), TiC-10wt%Ni-C (18.4% wt% C), TiC-10wt%Ni (19.8wt% C) and TiC-10wt%Ni (16.5 wt% C) respectively; processed according to the information in Table III and whose densification profiles are seen in Fig. 16. The change in carbon content which accompanied the various processing treatments (adding carbon or pretreating in hydrogen) results in different equilibrium phase regions for these compositions with accompanying changes in solidus temperature and eutectic reaction. These changes can be directly correlated to differences in liquid phase densification kinetics. While points 1-4 are located on an 870°C isothermal section of the ternary, conclusions drawn about the higher temperature eutectic reactions are valid as the liquidus projections and the boundaries between three phase fields containing liquid on the invariant plane are independent of temperature.

Composition 1, TiC-10wt%Ni with no additional carbon and no hydrogen heat treatment, is at the equilibrium composition boundary between the gamma-delta-carbon ternary and the gamma-delta quasi-binary. Under equilibrium conditions this composition is expected to form a liquid phase between the ternary eutectic at 1270°C and the quasi-binary eutectic at 1307°C. The 1290 C liquid phase formation observed in the high temperature SEM is in good agreement with the solidus reported by Stover and Wulff. Liquid would form in equilibrium with both gamma and delta and with increasing temperature enter a liquid-delta phase region. With a slight increase in carbon content up to the phase boundary between the three phase fields containing liquid on the invariant plane, the equilibrium change in phases would be
similar with the exception of equilibrium of delta-gamma-and carbon below the 1270°C eutectic. Liquid phase would form as with composition 1, in equilibrium with both gamma and delta with solid gamma entering the liquid phase with a small increase in temperature. Such an equilibrium reaction would be expected with the TiC-10wt% Ni-C (17.6wt% C) composition whose shrinkage profile is seen in Fig. 16. It can be seen that the small change in carbon content and resulting small change in eutectic reaction leads to little change in densification kinetics compared with samples to which no carbon had been added. The 1290°C liquid phase formation for this composition is higher than the reported ternary but can be explained on the basis of both accuracy of temperature measurement and kinetics of attaining equilibrium conditions.

As the carbon content continues to increase the equilibrium phases at the eutectic change from liquid in equilibrium with delta and gamma to liquid in equilibrium with delta and carbon. The boundary between these three phase fields (dashed lines in Fig. 24) are compositions where at the eutectic temperature liquid forms in equilibrium with delta phase alone. At the 1270°C eutectic, compositions 2 and 3 will form liquid in equilibrium with carbon and a carbon rich titanium carbide. In Fig. 16 it is seen that a marked decreased in densification accompanies the increase in carbon content and resulting change in eutectic reaction. The temperature range over which the liquid-carbon-delta phase region is stable is strongly dependent upon carbon content due to the very high carbide-carbon eutectic at 2776°C. For composition 2, very near the three phase region boundary, the carbon may exist in equilibrium with liquid and delta for
only a small range of temperature before the carbon enters the liquid phase solution. In comparison, composition 3 is likely to have a carbon-liquid-delta phase region stable over hundreds of degrees. For the sintering of runs of this study, particle compacts with compositions corresponding to composition 3 are expected to have solid carbon present throughout the sintering runs to 1360°C. For this same composition, in the high temperature SEM the identification of liquid phase by its flow through the solid carbide particle compact was not observed.

Carbon analysis of titanium carbide-nickel powder compacts indicated a progressive decrease in carbon content with increasing time and temperature of presintering heat treatment in flowing ultrapure hydrogen. For TiC-10wt% Ni samples treated at 800°C for one hour, the final total carbon content was 16.5 wt%. In Fig. 24 point number 4 represents this composition which is located at the convergence of the gamma-delta quasi-binary, gamma-delta-TiNi₃ ternary, and TiNi₃-delta carbide region. Three equilibrium phase regions exist within less than one atomic percent change in carbon content at this approximate composition. For compositions within the quasi-binary, liquid phase is expected at temperatures between the ternary eutectics at 1270°C and 1295°C and the quasi-binary eutectic at 1307°C. Again the 1290°C temperature of liquid phase formation observed in the SEM for compositions which after hydrogen heat treatment were in this phase region (16.7-17.2 wt% carbon) agrees well with these expected solidi. Within the gamma-delta-TiNi₃ ternary, liquid will form at 1295°C in equilibrium with either gamma and delta or TiNi₃ and delta. While gamma in equilibrium with liquid and carbide exists over
a small temperature range (1295-1307°C), TiNi₃ may exist in equilibrium with liquid and carbide up to 1390°C. For lower carbon content compositions within the TiNi₃-delta phase region, liquid would not form until the solidus temperature of 1390°C. The 1355°C liquid phase formation observed for particle compacts of composition 4 within the high temperature SEM corresponds with the higher eutectic in this region.

Samples of TiC-30 wt.% Ni treated in hydrogen at 800°C for 1 hour which did not show liquid phase in the SEM and untreated samples were analyzed by x-ray diffraction. No TiNi₃ phase which might have caused the higher solidus temperature was detected in the hydrogen treated sample. For both treated and untreated samples nickel peaks were not detected; even after heating to only 1220°C. A peak was observed which corresponded approximately with a nickel solution containing titanium. It is concluded that this peak is due to a nickel-carbon-titanium gamma phase.

Comparison of the equilibrium phase diagram for the Ni-Ti-C system with the densification of titanium carbide-nickel compacts suggests the presence of free carbon in equilibrium with the liquid and carbide phases greatly inhibits densification. Likewise, with decreasing carbon content, the formation of TiNi₃ as indicated by the ternary would explain the change in observed liquid phase formation temperature and subsequent decrease in densification. For hydrogen treated samples, however, wetting studies indicate that increased sensitivity of carbon deficient carbides to oxygen contamination makes explanation of densification behavior more complex.
3. Wetting Angle Measurements in the TiC-Ni System

Wetting at high temperatures is an extremely complicated phenomena in which chemical reactions between different phases plays a decisive part.

The observations made during the sessile drop experiments on various TiC-Ni systems in vacuo are summarized in Table VI. The heating rate for the wetting studies was approximately the same as used for the sintering runs i.e. 8 degrees/min.

<table>
<thead>
<tr>
<th>SYSTEM</th>
<th>OBSERVED EUTECTIC MELTING</th>
<th>CONTACT ANGLE (TEMPERATURE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC-Ni</td>
<td>1280°C</td>
<td>20 (1320°C)</td>
</tr>
<tr>
<td>TiC-Ni H2 treated 800°C 2 hours</td>
<td>1280°C</td>
<td>Initially 50 going to 15 in ~15 min. (1320°C)</td>
</tr>
<tr>
<td>TiC-Ni H2 treated 800°C 2 hours</td>
<td>1345°C</td>
<td>&lt;15 in high temp. SEM (quenched from 1345°C)</td>
</tr>
<tr>
<td>TiC-Ni+C (&gt;2wt% added C)</td>
<td>1260°C</td>
<td>80 (1300°C)</td>
</tr>
</tbody>
</table>

4. Influence of Hydrogen, Oxygen and Carbon Content on Wetting

The results of previous wetting investigations support these observations and suggest an interpretation of the variations measured. Humenik and Parikh \(^{20}\) investigated the wettability of TiC by Ni in various atmospheres. They measured contact angles of 17, 30, and 32 degrees for Ni on TiC at 1450°C in hydrogen, vacuum (10^-5 torr), and helium respectively. An influence of dissolution of TiC into Ni was pointed out in the study of Humenik and Whalen. \(^{21}\) They compared a
30 degree angle in vacuum with an initial 4 degree angle formed as liquid nickel was dropped onto a TiC surface.

Samonov et al.\textsuperscript{22} investigating the reactions of iron group metals on transition metal carbides measured a contact angle of $23 \pm 2$ degrees for Ni on TiC at $1450^\circ$C in vacuum ($5 \times 10^{-5}$torr). This value is in excellent agreement with the results of this study where an angle of 20 degrees was measured under similar conditions.

Ramqvist\textsuperscript{23} made a thorough study of the wetting of metallic carbides by liquid nickel, cobalt, iron and copper in vacuo ($10^{-5}$torr). Part of his investigation dealt with the effects of carbon deficient structures on wetting characteristics. To achieve decarburization wet hydrogen annealing was employed for some of his samples. His results for the wetting of TiC by nickel as a function of carbon content are shown in Fig. 25. The wetting angle, $\theta$, is seen to be strongly dependent upon carbon content varying from $\theta = 22$ degrees for TiC\textsubscript{1.0} to a wetting condition of $\theta = 0$ degrees for TiC\textsubscript{0.49}. Eutectic melting in the TiC-Ni system was reported at a temperature of $1340^\circ$C and measurements of wetting were taken at $1380$ C. No explanation was given for the unexpectedly high eutectic melting nor was there any indication of changes in the eutectic temperature with changes in stoichiometry.

Ramqvist related the change in wetting with the change in heats of formation of the carbides. In general, Ramqvist found in his study more stable carbides are wet less by metals. The stronger interatomic bonding in the more stable carbides was explained as leading to a higher liquid-solid interfacial energy and thus poorer wetting.
Based on the systematic relationship determined between wetting behavior and electronic structure, Goretzki et al. explain the similar wetting results of copper on refractory carbides of varying stoichiometry. Experimental measurements of the density of states, the energy distribution of bonding electrons, showed that an increase in this function corresponds with a decrease in wetting angles of copper on TiC\textsubscript{x}, ZrC\textsubscript{x}, and mixed carbides and nitrides in vacuum (10^{-7} torr). The improved wetting is viewed as a decrease in the interfacial energy between solid and liquid as unsaturated valence levels interact.

While the study of Goretzki et al. supports the results of Ramqvist, the complexity of TiC\textsubscript{x} - Ni systems as shown in the ternary and the kinetic analysis of reactions with varying carbide stoichiometry complicates the explanation of wetting phenomena. Wetting in the case of compound formation can be a result of the nature of the physical configuration of phases; isolation of the liquid from direct contact with the reacting solid being possible.

Tahtinen and Tikkanen stress the importance of oxygen potential on the wetting behavior of Ni on TiC. Varying oxygen potential in their experiments with H\textsubscript{2} - H\textsubscript{2}O mixtures, they observed at 1400°C wetting angles of 12 and 42 degrees for oxygen partial pressures of p = 10^{-4} torr and p = 10^{-2} torr, respectively. At an oxygen potential of p = 10^{-10} torr no melting was observed at a temperature of 1400°C. These results were attributed to the increasing severity of passivation of the carbide surface due to the intense chemisorption of oxygen. In this same study the wetting angle of Ni on TiC at 1400°C in a vacuum of \textasciitilde10\textsuperscript{-6} torr was reported to be 19 degrees.
This value is again in good agreement with results of this study measured in a vacuum of low oxygen potential.

It is apparent from the work of this investigation and past studies that the wettability of titanium carbide by nickel and thus the liquid phase sintering in this system, is dependent upon the stoichiometry of the carbide, amount of excess carbon in the system, amount of excess carbon in the system, oxygen potential and presence of hydrogen in processing. The mutual dependence of these factors, however, complicates an isolation of their separate effects.

The enthalpies of formation of titanium carbides and oxycarbide were determined by Morozova et al. They reported an approximately linear decrease in the enthalpy of formation of the carbide with decreasing carbon content. The enthalpies of formation of oxycarbides were found to be higher than the extrapolated values of carbides containing the same amount of carbon (Table VII).
TABLE VII

<table>
<thead>
<tr>
<th>COMPOUND</th>
<th>ENTHALPY OF FORMATION $-\Delta H$ kcal.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC 0 .23 .12</td>
<td>24.5 ± .2</td>
</tr>
<tr>
<td>TiC 0 .42 .12</td>
<td>39.8 ± .4</td>
</tr>
<tr>
<td>TiC 0 .46 .11</td>
<td>39.7 ± 1.5</td>
</tr>
<tr>
<td>TiC 0 .61 .08</td>
<td>42.8 ± 1.1</td>
</tr>
<tr>
<td>TiC 0 .74 .06</td>
<td>47.1 ± 1.6</td>
</tr>
<tr>
<td>TiC .79</td>
<td>43.7 ± .5</td>
</tr>
<tr>
<td>TiC .91</td>
<td>49.4 ± 2</td>
</tr>
<tr>
<td>TiC</td>
<td>55.3 ± 3</td>
</tr>
</tbody>
</table>

These values are indicative of the problems in attaining carbide samples which are oxygen free. In discussing the preparation of carbides Storms \(^{18}\) lists the stability of oxycarbides in decreasing order as Group IV, Group V, and Group VI. He further states that Group IV (Ti, Zr, Hf) carbides will become contaminated with oxygen impurity during low temperature (1000-2000°C) heating unless vacuum is better than $\sim 10^{-6}$ torr.

The wettability of Ni on titanium carbides reported by Ramqvist might be questioned on the basis of the influence of oxygen in his system (vacuum $\sim 10^{-5}$ torr). Following the arguments of Tahtinen and Tikkanen, the higher than expected eutectic melting temperatures might be explained as a result of oxygen passivation of the carbide.
surface. The lower wetting angles for these carbon-deficient structures, however, would be contrary to the results predicted by Tahtinen and Tikkanen's study. Moreover, the work of Goretzki et. al. gives supporting evidence to increased wetting for increasingly carbon deficient titanium carbide.

Auger analyses were performed on both untreated and hydrogen treated TiC-Ni compacts after a partial sintering to 1200°C in the high temperature SEM to determine the effects of this processing on oxygen content. The elemental analyses thus obtained are shown in Fig. 26. The plot is one of the derivative of the intensity peak for the characteristic Auger electrons emitted for the indicated elements. Although quantitative results are not possible from the fracture surfaces of the samples used; the spectra indicate a higher amount of oxygen in the TiC-Ni compact that underwent no hydrogen treatment. Oxygen content is more prevalent at the carbide surface. After one minute sputtering to remove surface layers a reduced oxygen content was detected in the particle compact which did not undergo hydrogen treatment and no oxygen was detected in the sample which had been treated in hydrogen at 800 C for one hour. For the fractured surface of the hyrdogen treated sample the Auger carbon peak is characteristic of free carbon. After sputtering, the carbon peak of a carbide is evident with a higher carbon to titanium peak ratio than samples which were not hydrogen treated. This is contrary to expectation as hydrogen treatment resulted in reduced carbon content of the samples. As no standards are available for the comparison of these peaks to carbides and oxycarbides conclusive statements about changes in stoichiometry cannot be made.
The reduction of a surface oxycarbide indicated by the Auger spectra may alter the solid-liquid relative interfacial energies leading to improved wetting. Goretzki et al.\textsuperscript{25} state that substitutional solution of oxygen in carbides of the fourth group would cause limited increase in the wettability of liquid metals. This is based on the observed wetting behavior of solid solutions of ZrC and ZrN and the assumption that the same influence would be expected in the exchange of nonmetallic component in the carbide-oxide systems. No conclusive studies have detailed the effects of oxygen content in oxycarbides on liquid metal wettability. The findings of Tahtinen and Tikkanen do indicate that in increasingly oxidizing environments wetting is decreased. Such a result might be intuitively expected based on the oxidation behavior of TiC. In an atmosphere of sufficient oxygen potential a protective rutile (TiO\textsubscript{2}) may form on titanium carbide. Humenik and Kingery\textsuperscript{28} have reported a wetting angle of 105 degrees for Ni on TiO\textsubscript{2} in vacuo. The progressive decrease in wetting with increasing oxygen contamination can not be assumed, however, due to basic structural differences between oxycarbides and rutile.

While Tahtinen and Tikkanen explain their results by the sole influence of oxygen potential, it may be that the establishment of oxygen potential by H\textsubscript{2}-H\textsubscript{2}O mixtures is critical to their findings.

Titanium carbide is reported structurally stable in static hydrogen up to 2400\textdegree{}C. Storms, however, reports that in flowing H\textsubscript{2} extensive decarburization can occur and result in compositions below TiC\textsubscript{1.0}. May and Hoekstra\textsuperscript{29} in addition note that titanium carbide is volatile in the presence of water vapor but give no data for interpretation. Wet hydrogen annealing was used to decarburize samples
in Ramqvist's study. The dissolution of hydrogen in defect structure carbides reported by Storms could cause further complications in the comparison and interpretation of wetting studies.

In the wetting study of Tahtinen and Tikkanen, the decarburization of titanium carbide in the $H_2 - H_2O$ atmospheres may affect the wetting by nickel. From the results of this study it is evident that in a system of low oxygen potential, treatment in hydrogen increases wettability from 22 degrees to 15 degrees. These results would compare with Tahtinen and Tikkanen's measurement of a 12-degree wetting angle in the system of lowest oxygen potential. The results of Ramqvist indicate 12-15 degree wetting angles for nickel on carbides of stoichiometry TiC$_{0.70}$.

Ideally, sessile drop experiments should be performed on single crystals. Due to their extremely high melting temperatures, single crystals of titanium carbide are extremely difficult to produce. Interpretation of wetting experiments with polycrystalline substrates must consider the effects of liquid movement along grain boundaries on wetting angles observed. In the copper-silver system Sharps et al. have observed contact angles between 2 and 19 degrees for eutectic compositions on polycrystalline copper solidus. The range in contact angles was seen to be a function of the greater movement of liquid along grain boundaries in small grain samples.

Examination of the cross section of the sessile drop formed by hydrogen treated Ni on hydrogen treated TiC (Fig. 27) shows extensive intergranular penetration of TiC by Ni. The dissolution of TiC into Ni melt results in the destruction of the flat substrate surface (Fig. 27A). Liquid can be seen to have penetrated vertically more than
halfway through the substrate and to have advanced beyond the periphery of the nickel drop (Fig. 27B). At the interfacial region, carbide precipitated from the liquid on cooling can be seen. The porosity of the carbide, seen at the limit of liquid penetration, contributes to capillary flow and grain boundary penetration (Fig. 27C). As the wetting experiments of this study were performed on carbide substrates of equivalent grain size, changes in the extent of liquid penetration of grain boundaries with changes in processing could contribute to the observed differences between wetting in systems that were hydrogen treated.

As already stated, it is difficult to isolate the effects of oxygen contamination from the influence of hydrogen decarburization of TiC. The wetting results of this study indicate that pretreatment in hydrogen increases wetting although the attainment of the lower wetting angle takes greater time. The results of Ramqvist indicate that such an increase in wetting would be expected from carbide decarburization. Carbon analysis of hydrogen-treated samples showed decreasing carbon content and thus supports this as a possible explanation. The Ni-Ti-C ternary phase diagram reveals that with decreasing carbon content reactions between Ni and carbides can lead to compound formation. Kinetics of such reactions at the solid-liquid interface could explain the time dependence of the attainment of the lower wetting angle.

The results of Ramqvist indicate that the decrease in wetting angle of Ni on TiC after hydrogen treatment observed in this study is an effect of oxygen removal from the carbide structure. Auger analysis supports this argument. The observation in this study of increased temperatures of eutectic melting is similar to the lack of melting in
the TiC-Ni system in an atmosphere of \( H_2 - H_2O \) yielding \( P_0 = 10^{-10} \) torr in Tahatinen and Tikkanen’s work.

The eutectic temperature was not seen to change for hydrogen-treated and untreated samples in the wetting experiments of this study. In the high temperature stage of the SEM, however, hydrogen treatment was seen to reduce the rate of shrinkage for TiC-Ni compacts. For hydrogen treatment identical with that of samples in wetting studies, liquid phase formation was inhibited to a temperature of \( \approx 1360^\circ C \). The difference between the wetting experiments and the high temperature SEM sintering runs may be a result of the very low oxygen potential of the furnace of the wetting study. A wetting experiment was performed in the SEM with hydrogen treated Ni and a small hydrogen treated substrate of TiC. This system also exhibited a high eutectic temperature of \( \approx 1345^\circ C \). The wetting angle could not be determined in the microscope due to the perpendicularity of the sample to the scanning beam. The wetting angle was observed on the quenched sample to be low although a measurement could not be made due to the small size of the sample and liquid phase penetration into the substrate.

The results of this study indicate that it is not oxygen potential alone which results in inhibited eutectic reaction. Hydrogen must be present in the processing. It is unclear what the role of hydrogen is however. In the phase diagram of the Ti-C-Ni system determined by Stover and Wulff, an increase in the solidus temperature as the system moved from the delta-gamma-TiNi\(_3\) region to the delta-TiNi\(_3\) region would correspond with the changes observed in temperatures of liquid phase formation and the change in carbon content of particle compacts.
The progressive decrease in sinterability with hydrogen treatment is not fully understood. According to the results of this study and previous studies the decrease in wetting angle with hydrogen treated material would be expected to lead to increased densification. The observed time dependence of wetting seen in hydrogen treated material, however, would support the reduced densification rates measured in this study. It is possible that hydrogen treatment of micron size particles shows this transient wetting behavior to a greater degree. The explanation of this transient wetting behavior is not fully known. The results of this study and previous wetting studies suggest two possible causes. First, decarburization of titanium carbide by hydrogen treatment results in the reaction of the decarburized surface with nickel to form a boundary to liquid phase formation. Observed liquid phase formation and reference to the Ti-Ni-C ternary show TiNi$_3$ is the possible barrier phase. X-ray analysis could not detect this compound however. Second, decarburization of the carbide results in greater affinity for oxygen in the vacuum environment of the SEM and leads to a surface oxycarbide which forms a passivating barrier to eutectic reaction. The extent of oxycarbide formation would be dependent upon the initial degree of hydrogen treatment through increased surface decarburization. The Auger spectra of samples heated to 1200°C would not support this explanation, however.

The influence of hydrogen treatment on wetting behavior as observed in the wetting experiments of this study can be interpreted by wetting theory. The balance of surface forces exerted on a liquid drop on a solid surface if stable or metastable chemical equilibrium exists is expressed as $(\gamma_{sv} - \gamma_{sl}) = \gamma_{lv} \cos \theta$. The value of $\gamma_{sl}$
will lie between $\gamma_{sv}$ and $\gamma_{lv}$ and the reduction of the larger $\gamma$ by formation of $\gamma_{sl}$ will not exceed the smaller. For the formation of an acute angle as in the case of Ni on TiC, $\gamma_{sv} > \gamma_{sl} > \gamma_{lv}$. The surface energy of TiC was calculated by Ogorondikov et al.\textsuperscript{30} from atomic bond models. They determined a value of 4070 erg/sq. cm. for a random solid surface. Warren calculated a titanium carbide surface energy from the degree of contact of spherical particles in a liquid matrix and wetting data. He determined the solid-vapor surface energy of the carbide to be 2215+200 ergs/sq. cm. The surface tension of Ni at 1460 C is 1780 ergs/sq. cm.\textsuperscript{23} which is the right order of magnitude to obtain an acute angle on TiC.

The decarburization and/or removal of oxygen from an oxycarbide surface leads to increased wetting as observed in this study. If we assume equilibrium conditions, hydrogen treatment would lead to a decrease in wetting angle through an increase in the solid-vapor surface energy, decrease in solid-liquid surface energy or combination of these factors. The results of Tahtinen and Tikkanen indicate that the solid-vapor interfacial energy of TiC decreases with absorption of oxygen. Following this reasoning, the hydrogen treatment of this work which resulted in a removal of oxygen from the system could lead to the higher $\gamma_{sv}$ and thus reduced wetting angle. The fact that the observed wetting of hydrogen treated titanium carbide and nickel is time dependent indicates a reaction is occurring. If this is the case, a dynamic situation exists and the driving force for wetting can be expressed as $\gamma_{sv} - (\gamma_{sl} + d\Gamma)$, where $d\Gamma$ is the free energy change of the reaction per unit surface per unit time.
Pask and Tomsia\textsuperscript{10} and Sharp et al.\textsuperscript{11} have concluded that if the solid is an active participant in the reaction (i.e. it changes composition) a decrease in the effective solid-liquid interfacial energy can lead to a spreading condition. These investigators have also stated that an interfacial reaction in which the solid is a passive participant (i.e. no change in composition) does not contribute to driving force for wetting regardless of the magnitude of the free energy change. This wetting theory suggests that the observed decrease in wetting angle of hydrogen treated nickel on hydrogen treated titanium carbide results from a change in chemistry of the constituents leading to a reaction in which the solid composition is altered. A development of the possible reactions is necessary.

While Stover and Wulff have reported negligible solubility of nickel in titanium carbide, an increase in even a trace solubility of Ni in hydrogen treated titanium carbide could lead to improved wetting. A solubility of hydrogen in both nickel and titanium carbide also creates the possibility of the alteration of the carbide composition by interdiffusion of hydrogen from the liquid nickel.

Reference to the Ti-Ni-C ternary has shown reactions between carbon deficient titanium carbide and nickel are expected. Specifically, decarburized TiC can react with nickel to form TiNi\textsubscript{3}. Although not identified as a phase in the sintered compacts, the formation of a limited interfacial layer of TiNi\textsubscript{3} could contribute to a wetting condition. If the mechanism of formation was followed by rapid solution into the liquid, this phase would not be detectable but the reaction would make the solid an active participant. While existence of a carbide \(\text{Ni}_3\text{C}\) has been reported, it is considered
unstable at temperatures above 300°C and under conditions of this study not influential.

5. Influence of Additional Carbon on Wetting

No studies which correlate effects of initial carbon concentration in nickel on the metals wettability on titanium carbide have been found in the literature. Samsonov\textsuperscript{22} reported a marked adverse effect of carbon in nickel on the wetting of zirconium carbide. An addition of 5 wt.% carbon to nickel increased the angle of contact from 23 degrees for pure nickel on ZrC to 103 degrees. The similar electronic structure in Group IV metal carbides leads to similar wetting behavior by metal liquids. Samsonov's observation can therefore be considered support of the findings of this study.

The cross section of a titanium carbide substrate which underwent no previous heat treatment and a carbon saturated nickel drop in which $\theta$ was measured as 80 degrees is seen in Fig. 28A. Near the interface of the nickel drop a dark layer is apparent. At higher magnification this area is seen to be an eroded section with liquid phase present on each side (Fig. 28B). Probing of regions of this area by x-ray spectroscopy (EDAX) revealed no peaks for elemental identification. Within the quenched drop a dendritic precipitate and an irregular black phase are seen. X-ray probing of the dendritic structure showed the presence of titanium while the black phase again produced no peaks. It is concluded that the interfacial region and black phase are carbon. The dendritic structure is titanium carbide precipitated from the nickel melt. The erosion of the interfacial region was a result of polishing.
The 1260°C liquid phase formation observed for this system is in good agreement with the 1270°C eutectic reported by Stover and Wulff for the TiC-gamma-carbon ternary. At the interface beneath the carbon layer, penetration of liquid into the substrate down grain boundaries is observed. The mechanics of formation of this interfacial structure can be postulated.

The beginning nickel compact consisted of particles of nickel coated with carbon. The carbon content exceeded the eutectic concentration so that solid carbon existed in the drop throughout the wetting experiment. During heating to the liquid phase formation temperature sufficient titanium and carbon diffused into the nickel compact to result in eutectic melting. Upon liquid phase formation, the solid carbon in the nickel rapidly accumulated near the solid-liquid interface. The liquid assumed the 80 degree wetting angle without measurable transition through other wetting configurations. Liquid phase which originally formed near the titanium-carbide sample penetrated the sample as a result of capillary flow and dissolution along grain boundaries. This penetration is, however, much less pronounced than in the hydrogen treated sample. The difference in intergranular penetration is due to the change in solubility of TiC in the nickel melt saturated with carbon.

In a study of the thermodynamics of carbon in nickel based multicomponent solutions, Bradley determined a decrease in the carbon activity coefficient and decreased solubility of carbon in solutions in which titanium carbide exists in equilibrium.

The dependence of titanium carbide dissolution on carbon concentration has been shown in the grain growth studies of Exner
et al.\textsuperscript{14} and Humenik and Whalen\textsuperscript{21}. In these studies carbide grain growth for samples sintered on graphite was decreased in comparison to samples sintered on alumina.

Assuming the micrograph of the wetting sample is representative of high temperature phase distribution, the existence of carbon in the nickel melt and dissolution of titanium carbide results in an accumulation of carbon near the solid-liquid interface. The wetting angle measured becomes one of a liquid solution of nickel, titanium and carbon on carbon.

Humenik and Whalen\textsuperscript{21} reported the effects of carbon in nickel on wettability with graphite in vacuum at 1455°C. These results are given Table VIII.

<table>
<thead>
<tr>
<th>INITIAL CARBON CONC.</th>
<th>EXPERIMENTAL CONDITIONS</th>
<th>CONTACT ANGLE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni (no carbon)</td>
<td>1</td>
<td>59 degrees</td>
</tr>
<tr>
<td>Ni (no carbon)</td>
<td>3</td>
<td>82 degrees</td>
</tr>
<tr>
<td>Ni (2.3wt% C)</td>
<td>1,2,3</td>
<td>145 degrees</td>
</tr>
</tbody>
</table>

1. Pure liquid metal dropped onto graphite
2. Alloy heated in contact with graphite
3. Pure metal or alloy rapidly heated (50 C/min) in contact with graphite
Weisweiler and Mahadevan\textsuperscript{33} refer to Naidich and Kolesnichenko's study of the wettability of graphite by carbon saturated melts and pure metal melts at 1550°C. For pure nickel on graphite an angle of 57 degrees was measured while for the eutectic melt an angle of 115 degrees was observed.

Humenik and Whalen\textsuperscript{21} also reported similar findings in the wetting of graphite by iron-carbon alloys. The contact angle Fe-C alloys on graphite is dependent upon the amount of carbon in the iron solution. As the carbon content increases to a saturated solution the contact angle progressively increases.

The wetting of both nickel and iron on carbon has been explained by the reduction in the solid-liquid interfacial energy due to dissolution into the liquid phase resulting in decreased wetting angles. As previously mentioned, recent wetting theory\textsuperscript{10,11} has concluded that a contribution to the driving force for wetting due to chemical non-equilibrium conditions occurs only when the solid is an active participant in the reaction. The wetting behavior of nickel and iron on graphite would be compatible with this theory if the metastable phase Ni\textsubscript{3}C and Fe\textsubscript{3}C were forming thus making the solid an active participant. Further work on these systems would be valuable in developing wetting theory for systems in which interfacial compounds are formed.

Studies on the effects of carbon\textsuperscript{34} and metallic alloying elements\textsuperscript{35}, including titanium, on the surface tension of liquid nickel solutions indicates little change with measured $\gamma_{lv}$ of solutions being slightly lower than the pure metal. These findings, combined with the observations of wetting of metals on graphite
support the conclusion that the observed wetting behavior of carbon saturated nickel on titanium carbide resulted from the formation of an interfacial layer of carbon during the wetting experiment.

In the high temperature sintering runs, the progressive decrease in densification with increasing carbon concentration is explained by the progressive decrease in solubility of carbide in the liquid phase. The absence of an observable liquid phase in the TiC-10wt%Ni compact containing 19.8 wt% C results from the presence of solid carbon throughout the sintering run as explained by reference to the Ni-Ti-C ternary. The increase contact angle in the presence of carbon resulted in no observable liquid flow throughout the carbide particles. The reduced wetting of the carbide resulted in reduced solid-liquid interfacial area (Fig. 19). This factor combined with the decreased solubility of TiC in carbon saturated nickel to reduce the rate of mass transport through the liquid phase leading to reduced sintering rate.
IV. CONCLUSIONS

High temperature scanning electron microscopy has been used to study the shrinkage of titanium carbide - nickel composites. Sintering in this system is extremely sensitive to processing conditions. Additions of free carbon to titanium carbide - nickel compacts reduces shrinkage when sufficient carbon is added to result in the presence of carbon after liquid phase has formed. Shrinkage is reduced by the combined influence of the decreased solubility of titanium carbide in the liquid phase leading to reduced rates of mass transport through the liquid and by the decreased wettability of the carbon saturated liquid on the solid. This decreased wettability results in decreased interparticle forces between solid particles and decreased solid-liquid interfacial area with corresponding increase in the solid-solid interfacial area and slower solid state kinetics.

Presintering heat treatment of titanium carbide - nickel compacts in hydrogen adversely affects liquid phase shrinkage. Titanium carbide is difficult to prepare without some oxygen contamination. The influence of hydrogen treatment is then complicated by the loss of both oxygen and carbon from the carbide structure. The dynamic change in wetting angle and the increased liquid phase formation temperature which results indicates an interfacial barrier to reaction or the formation of a compound at the nickel-carbide interface. The analysis of compositional changes of titanium carbide - nickel compacts after hydrogen treatment and the Ti-Ni-C ternary indicates the possible formation of TiNi$_3$ which would support the increased temperature of liquid phase formation in these systems. The presence of TiNi$_3$ could not be detected, however. The mechanism leading to reduced
densification in the titanium carbide - nickel has not been identified. More detailed studies on the stability of carbides and oxycarbides in dry hydrogen and the nature of reactions between carbon deficient carbides and nickel are required.
REFERENCES


11. P. Sharps, A.P. Tomsia, and J.A. Pask, "Wetting and Spreading in the Cu-Ag System," to be published.


ACKNOWLEDGEMENTS

Through the course of this work, Professor Joseph A. Pask has been a guiding source of scientific interpretation. With greatest sincerity I wish to express my respect and my gratitude. He has been a true teacher to me.

This work was begun under the guidance of Professor Richard M. Fulrath. I am grateful that I had the opportunity to know such a man. He gave his students much and his influence and memory will always be with them.

I also wish to thank Professor Donald R. Olander and Professor Alan W. Searcy for their critical evaluation and their helpful discussions of this study.

My special thanks go to Phil Flaitz and V. K. Nagesh for the many hours given me which have added to this work.

Finally to my parents, who have been such a source of strength in these past years and throughout my life, my love and appreciation.

This work was supported by the Director, Office of Basic Energy Sciences, Division of Materials Sciences of the U.S. Department of Energy under Contract No. W-7405-ENG-48.
FIGURE CAPTIONS

Fig. 1. Physical configuration of a liquid on a solid under chemical equilibrium conditions.

Fig. 2. The Heady and Cahn model for the force between two solid spheres connected by a liquid bridge.

Fig. 3. Gressinger, Fishmeister, and Lukas model for force acting upon the solid-solid contact area between two spherical particles by surrounding liquid.

Fig. 4. The solid-liquid equilibrium dihedral angle.

Fig. 5. (A) Winding of Lucalox heating element with tungsten wire.
(B) Heating element with outside high purity alumina sleeve.
(C) Completed heating element with molybdenum radiation shielding.

Fig. 6. (A) High temperature SEM specimen stage with tungsten radiation and top cover plate removed.
(B) Fully assembled high temperature stage.

Fig. 7. (A) Specimen stage within the main stage of the SEM.
(B) Main stage with thermal suppression grid mounted.

Fig. 8. Set up for optical pyrometer calibration of the high temperature stage.

Fig. 9. High temperature stage heater power versus thermocouple temperature.

Fig. 10. Temperature calibration curve for high temperature stage at constant heating rate of 8 degrees/min.

Fig. 11. The Carbon-Titanium binary phase diagram.

Fig. 12. (A) TiC grains size separated 10 microns and below.
(B) Ni grains size separated 10 microns and below.
Fig. 13. (A) (C) Alumina spheres on TiC-10 wt.% Ni compact at 700°C. (B) (D) Same area of sample at 1300°C.

Fig. 14. Low magnification picture of SEM video image of TiC-Ni compact at 700°C.

Fig. 15. Influence of Ni content on shrinkage of TiC-Ni particle compacts.

Fig. 16. Influence of carbon content on densification of TiC-10 wt.% Ni particle compacts.

Fig. 17. Influence of carbon content on TiC-20 wt.% Ni particle compact densification.

Fig. 18. Influence of carbon content on TiC-30 wt.% Ni particle compact densification.

Fig. 19. (A) Polished TiC-10 wt.% Ni (17.3 wt.% C) compact after heating to 1360°C (13% total shrinkage). (B) Polished TiC-10 wt.% Ni (19.8 wt.% C) compact after heating to 1360°C (9% total shrinkage).

Fig. 20. Influence of hydrogen treatment on TiC-10 wt.% Ni compacts.

Fig. 21. Shrinkage of TiC-20 wt.% Ni compacts after varied hydrogen treatments.

Fig. 22. Effect of hydrogen heat treatments on TiC-30 wt.% Ni particle compact densification.

Fig. 23. Comparison of fracture surfaces of TiC-30 wt.% Ni compact without previous hydrogen treatment (A, C, E) to TiC-30 wt.% Ni compact with presintering hydrogen treatment (B, D, F) after heating to 1360°C.

Fig. 24. An 870°C isothermal section of the C - Ti - Ni ternary phase diagram.
Fig. 25. Wetting of TiC by Ni as a function of carbide stoichiometry.

Fig. 26. (A) Auger spectra of TiC-30 wt.% Ni compact after partial sintering to 1200°C.

(B) Auger Spectra of TiC-30 wt.% Ni compact hydrogen treated at 800°C for 2 hours after partial sintering in the SEM.

(C) Auger spectra of compact of (A) after 1 min. sputter.

(D) Auger spectra of compact of (B) after 1 min. sputter.

Fig. 27. (A) Cross section of sessile drop of hydrogen treated Ni on hydrogen treated TiC substrate.

(B) Penetration of Ni melt into TiC substrate.

(C) Limit of penetration of Ni melt illustrating substrate porosity.

Fig. 28. (A) Cross section of sessile drop of carbon saturated Ni on TiC (no hydrogen treatment, no added carbon)

(B) Interfacial region between Ni rich melt and TiC substrate.

(C) Region within Ni melt illustrating dendritic carbide and graphite precipitant.

(D) Region just below interface illustrating limited penetration of the melt into substrate.
Fig. 1
Fig. 4
Fig. 5
HEATING RATE, °C/MIN.

- □ 1.1
- ○ 3.8
- △ 8.6
- ▽ 13.0

HEATER POWER INPUT (WATTS)

THERMOCOUPLE TEMPERATURE (°C)

Fig. 9
HIGH TEMPERATURE STAGE CALIBRATION

CONSTANT HEATING RATE 8 DEGREES PER MIN.

OPTICAL PYROMETER TEMP. C

THERMOCOUPLE TEMPERATURE C

Fig. 10
Fig. 12

XBB 810-9320
Fig. 14
TiC-Ni COMPACTS INFLUENCE OF Ni CONTENT

Fig. 15

PERCENT SHRINKAGE

TEMPERATURE DEGREES C

XBL 812-8248
TiC-10Wt%Ni INFLUENCE OF CARBON CONTENT

PERCENT SHRINKAGE

TEMPERATURE DEGREES C

Fig. 16
TiC-20WT%Ni INFLUENCE OF CARBON CONTENT

PERCENT SHRINKAGE

CARBON 15.2% CONTENT

CARBON 16.1% CONTENT

TEMPERATURE DEGREES C

Fig. 17
Fig. 19
TiC-10wt%Ni INFLUENCE OF H2 TREATMENT

Fig. 20
TiC-20WT%Ni INFLUENCE OF H2 TREATMENT

NO HYDROGEN TREATMENT

H2 TREATMENT 800C 1/2 HR.

PERCENT SHRINKAGE

TEMPERATURE DEGREES C

Fig. 21
TiC-30wt%Ni INFLUENCE OF H₂ TREATMENT

TEMPERATURE DEGREES C

Fig. 22
Fig. 23
Processing Conditions

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Fig. 24
Fig. 26
Fig. 28
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