EFFECT OF UNCOMBINED CALCIUM AND MAGNESIUM ON THE
MALLEABILITY OF NICKEL ALLOYS

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ABSTRACT

Calcium and magnesium are added to many Ni-Cr-Fe alloys to improve their malleability. It is generally regarded that these elements operate by neutralizing embrittling impurities such as sulfur and oxygen. However, it is also known that an excess of uncombined calcium or magnesium can cause severe hot shortness. This paper identifies the specific mechanism causing the loss of ductility in calcium and magnesium treated alloys and defines processing factors which influence sensitivity to embrittlement.

The paper defines the solid solubility of magnesium and calcium in Ni-Cr-Fe alloys and catalogs the Ni-Ca and Ni-Mg intermetallic compounds. Extensive use of electron microprobe analysis was made in the phase identification. The effect of cooling rate during solidification and soaking time on the volume fraction and distribution of magnesium- and calcium-rich phases is also discussed.

The second section of this paper deals with the hot workability of alloys containing uncombined calcium and magnesium. The results obtained with a simple upset forging test are interpreted in terms of the volume fraction, morphology and melting point of the magnesium- and calcium-rich phases.

Introduction

For many years calcium and magnesium have been added to Ni-Cr-Fe alloys
to improve their malleability. It is generally regarded that these elements
operate by neutralizing embrittling impurities such as sulfur and oxygen.
Improved castability, oxidation resistance and mechanical properties have
also been reported and in some alloys a specific residual level of these
elements is required. However, in some alloys an excess of calcium or
magnesium results in severe hot shortness and, due to erratic recovery,
caution is necessary in treating alloys known to be particularly sensitive
to "overtreatment". Although the subject is of great importance for alloy
producers, it has been dealt with for the most part on a phenomenological
basis. This approach has led to practical treatment guidelines but modern
alloys are so complex that unnoticed factors and synergisms make a purely
empirical approach hazardous. To fill this apparent gap in our under-
standing of this subject the present program sought to identify the specific
mechanism causing the loss of ductility in calcium and magnesium treated
alloys and to define processing factors which influence sensitivity to
embrittlement.

Calcium- and Magnesium-Rich Phases in Nickel-Base Alloys

The Ni-Ca and Ni-Mg binary diagrams (Figs. 1,2) provide a basis for
understanding the behavior of these elements in more complex alloys.
Examination of these systems shows similarities; i.e., unlimited liquid
solubility, restricted solubility in solid Ni and presence of Ni-rich low-
melting intermetallic compounds. These compounds are extremely brittle and
at temperatures near their melting points they are subject to catastrophic
oxidation. Some phases, such as $NiMg_2$ and Ni_2Ca, are also severely attacked
when exposed to water.

Nickel is one of the few transition metals which alloys with Ca and Mg.
These elements are practically insoluble in pure liquid Cr, Mo, Nb and Ti,
have limited solubility in liquid Fe and Co, and form no intermetallic
compounds with any of them(5). The ternary Ni-Ca/Mg-transition metal
systems are similar in many respects. For the sake of brevity the Ni-
Ca/Mg-Fe systems will be used as examples in the following discussions.
Data on the important Ni-Ca/Mg-Cr and Ni-Ca/Mg-Mo systems will be presented
as needed for clarification.

The estimated liquidus surfaces for the Ni-Ca/Mg-Fe systems are shown in
(Figs. 3,4). Also, ranges of occurrence of the Ca- and Mg-rich phases in
solid Fe-Ni alloys are indicated. The phase distribution ranges in the
analogous Ni-Ca/Mg-Cr and Ni-Ca/Mg-Mo alloys are listed in Table I. The
diagrams were constructed from data collected on a large number of 10 kg
laboratory heats. The phase compositions were determined by electron
microprobe.

A number of points are evident from the ternary diagrams. No Mg- or Ca-
rich phase other than those present in binary Ni-Ca and Ni-Mg systems are
formed in either system. Further, all of the binary Ni-Ca and Ni-Mg phases
have been observed in Ni-Fe alloys. To a limited extent Fe can replace Ni
in all of these phases. The very low melting point of constituents formed
during solidification of Fe-Ni alloys is of great significance. The same
phases occur in the Ni-Cr and Ni-Mo systems but the ranges of occurrence
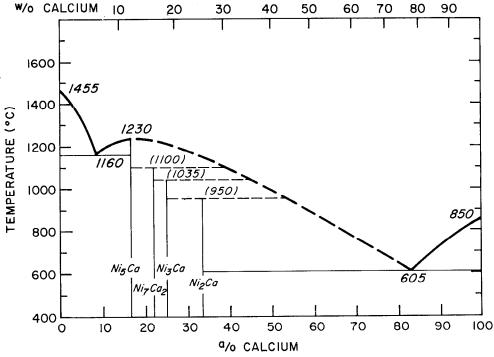are shifted (Table I).
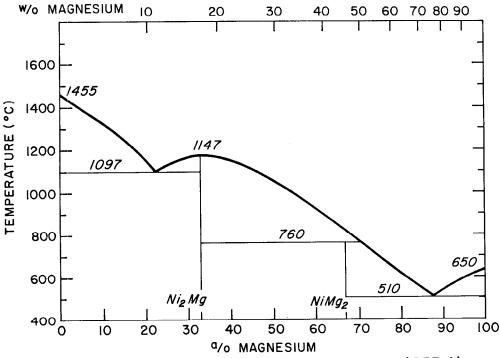
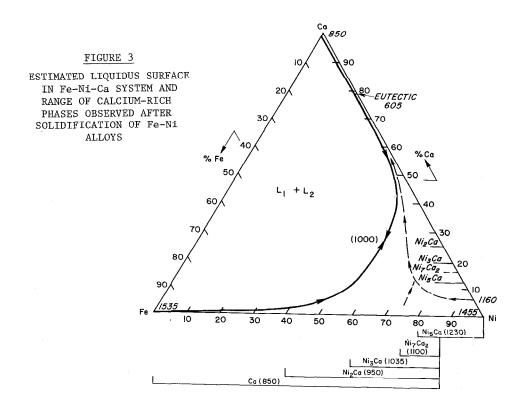FIGURE I - NICKEL-CALCIUM BINARY DIAGRAM. (REFS. I-3)
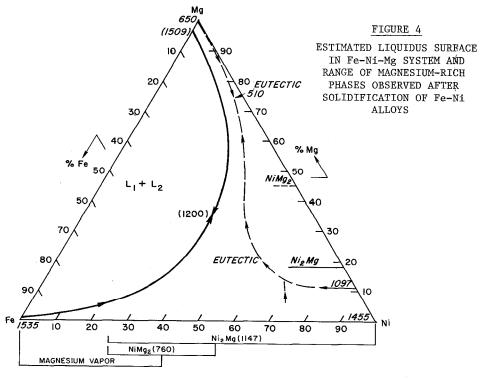

FIGURE 2 - NICKEL-MAGNESIUM BINARY DIAGRAM. (REF. 4)

FIGURE 3

ESTIMATED LIQUIDUS SURFACE IN Fe-Ni-Ca SYSTEM AND RANGE OF CALCIUM-RICH PHASES OBSERVED AFTER SOLIDIFICATION OF Fe-Ni ALLOYS

FIGURE 4

ESTIMATED LIQUIDUS SURFACE IN Fe-Ni-Mg SYSTEM AND RANGE OF MAGNESIUM-RICH PHASES OBSERVED AFTER SOLIDIFICATION OF Fe-Ni ALLOYS

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Table I

Approximate Range of Occurrence and Composition of
Calcium and Magnesium Phases in Ni-Fe, Ni-Cr and Ni-Mo Alloys*

		Calcium Phases				Magnesium Phases		
Base	Ni_5Ca	Ni_7Ca_2	Ni_3Ca	Ni_2Ca	Ca	Ni_2Mg	$NiMg_2$	Mg**
Ni-Fe	100-80	88-75	88-60	88-40	88-0	100-25	55-25	40-0
	8.0	(7.0)	6.0	3.6	Nil	15	(Nil)	Nil
Ni-Cr	100-85	92-80	92-70	92-55	92-0	100-35	(60-35)	(45)-0
	2.9	2.5	2.5	1.7	Nil	6.9	(Nil)	Nil
Ni-Mo	100-90	95-85	95-75	95-60	95-0	100-50	(65-35)	(50)-0
	Nil	Nil	Nil	Nil	Nil	Nil	(Nil)	Nil

*First entry - range of occurrence expressed as nickel content of
base alloy; second entry - maximum amount of Fe, Cr or Mo in
phase (w/o).
**Pure magnesium will almost always vaporize during solidification.

The prediction of Ca and Mg phases in multicomponent commercial alloys
is fairly straightforward. The phase distribution range for a complex
alloy can be estimated by converting the actual composition to an Fe equiv-
alent (F.E.) using the formulas:

$$F.E. \ (Ca) = \%Fe + 1.3\%Cr + 1.5\%Mo + 0.5\%Co$$
$$F.E. \ (Mg) = \%Fe + 1.1\%Cr + 1.2\%Mo$$

Elements such as W, Ta, Nb and Ti probably have effects similar to that of
Mo. Cu, Co in Mg treated alloys and probably Al are similar to Ni in their
effect on phase balance. It must be emphasized that these equations provide
only rough predictions of the phases to be expected in a given alloy.

While the equilibrium solubility of Ca and Mg in solid Ni is on the
order of 0.1 to 0.5 w/o, segregation during freezing is severe. In practice
Mg- and Ca-rich phases are visible at solute concentrations of 0.05% and
microprobe analyses of as-cast alloys indicate that the amount in solution
is 0.01% or less. Solubility in the solid is decreased by ternary solutes
such as Fe, Cr and Mo. The limited data for the Ni-Fe system obtained in
the present study are shown, (Fig. 5).

Since the Ca and Mg contents of the binary phases are dependent on the
matrix composition, it also follows that the volume fraction of the phases
will vary. The volume of second phases in Fe-Ni alloys containing 0.01%
uncombined Ca or Mg was calculated and plotted in Fig. 5. Note that in
each system the volume fraction increases with increasing Ni content. The
volume fraction of Mg-rich phase is zero in alloys containing less than 25%
Ni because all uncombined Mg was assumed to vaporize when the ingot solid-
ifies. The calculated volumes may appear trivial, but if present as an
intergranular film in an alloy with a grain diameter of 1 mm complete
coverage of the grain boundaries with a layer 0.4μm thick would result.

Microstructures of Ca-rich phases in selected Ni-base alloys are shown
in Fig. 6. Phase identification was made by microprobe analysis. Calcium
levels in the examples shown are higher than those of commercial alloys but
examination of a large number of alloys established that the morphology was
identical to the limit of second phase detectability. Note the strong
tendency of Ni_5Ca, Ni_7Ca_2 and Ni_3Ca to wet grain boundaries and form es-
sentially continuous films. On the other hand Ni_2Ca and especially pure Ca
were globular even where they were present at grain boundaries. Sample
preparation procedure proved to be quite important in revealing the structure
of the calcium-rich phases. After grinding on dry papers, diamond polish-
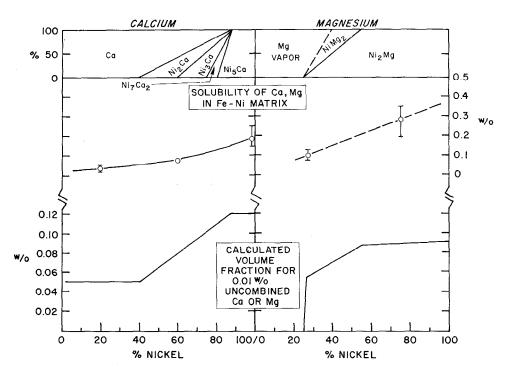
FIGURE 5 - DISTRIBUTION AND VOLUME FRACTION OF PHASES; SOLID SOL-
UBILITY FOR Fe-Ni ALLOYS.

PHASES

1. Ni_5Ca
2. Ni_7Ca_2
3. Ni_3Ca
4. Ni_2Ca
5. Ca
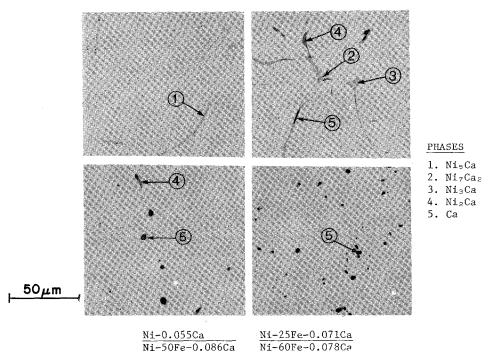
Ni-0.055Ca Ni-25Fe-0.071Ca
Ni-50Fe-0.086Ca Ni-60Fe-0.078Ca

FIGURE 6

CALCIUM-RICH PHASES FORMED DURING SOLIDIFICATION OF SELECTED Ni-Fe-Ca ALLOYS

ng in kerosene was employed. A final touch on 0.01μm alumina on a moistened lap was sufficient to bring out the microstructure. The polishing and etching procedures normally used for Ni alloys resulted in dissolution of the second phase. Hence it is understandable that these phases had previously escaped the notice of most metallurgists.

Microstructures of Mg-rich phases in Ni-base alloys are shown in Fig. 7. Grain boundary films of both the Ni_2Mg and $NiMg_2$ phases were observed only at relatively high Mg contents. Generally, when the Mg content was less than about 0.1% the particles were globular or irregular. The presence of Cr and Mo also seems to favor a more irregular, discontinuous phase structure (Fig. 7b). The phase $Ni_2(Mg_xC_{1-x})$ was also occasionally observed (Fig. 7d). This phase is unlikely to occur in commercial Ni-base alloys because it is suppressed by carbide stabilizing elements such as Cr and Mo.

PHASES

1. Ni_2Mg
2. $Ni \cdot (Mg_xC_{1-x})$
3. $NiMg_2$

50 μm

Ni-14Cr-0.19Mg   Ni-21Cr-19Fe-8Mo-0.69Mg
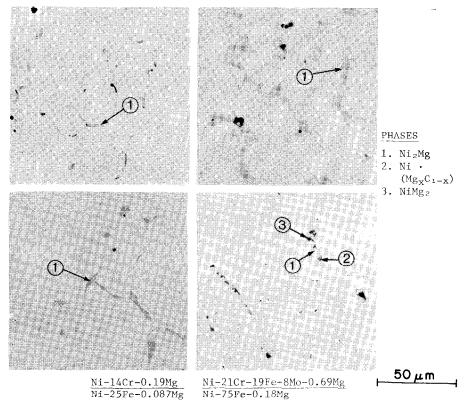Ni-25Fe-0.087Mg   Ni-75Fe-0.18Mg

FIGURE 7 - MAGNESIUM-RICH PHASES FORMED DURING SOLIDIFICATION OF SELECTED Ni-Fe-Cr-Mg ALLOYS

Malleability of Calcium and Magnesium Treated Alloys

As mentioned previously Ni-Ca and Ni-Mg phases are extremely brittle. Consequently, it is not surprising that alloys in which the second phase was readily visible in the microscope were cold short. However, it was felt that alloys containing such large volumes of Ca- or Mg-rich phases would also be hot short. Consequently, work was concentrated on defining the effect of these elements on hot workability. The scope of the potential hot shortness problem is illustrated in Fig. 8 which shows the melting points of the phases superimposed on their range of occurrence in Fe-Ni alloys. Clearly these phases would be liquid at the normal hot working temperatures of most commercial alloys.
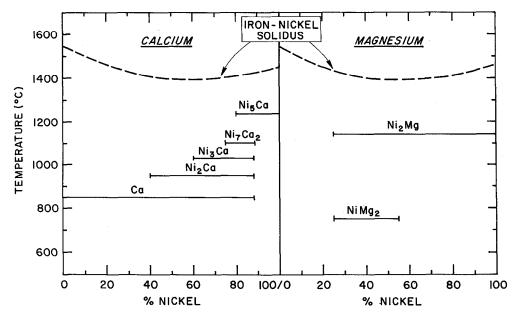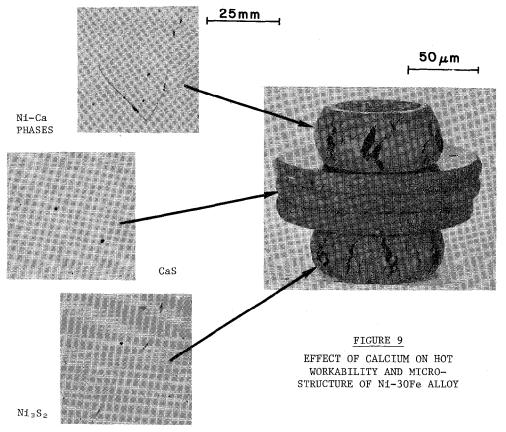
FIGURE 8 - MELTING POINT OF CALCIUM AND MAGNESIUM-RICH PHASES AND
THEIR REGION OF FORMATION IN IRON-NICKEL ALLOYS.

FIGURE 9

EFFECT OF CALCIUM ON HOT
WORKABILITY AND MICRO-
STRUCTURE OF Ni-30Fe ALLOY

The test of hot workability used in this study, although relatively crude, proved quite useful for screening a wide range of alloy compositions. The test specimen was a cast cylinder 65 mm high and 30 mm in diameter. The cylinders were soaked in air in a muffle furnace for one hour and then upset forged to the point where cracking occurred. Most of the alloys were prepared as series of split heats in which Ca or Mg additions were varied for a given matrix composition. Typical addition levels were 0.02, 0.04, 0.06, 0.12 and 0.25%. Forged cylinders for a Ni-30Fe alloy are shown in Fig. 9. This series contained 0.02% S to illustrate the role of Ca in alleviating the embrittling effect of S. A similar series with Mg additions gave comparable results. Sulfur was not added to most of the alloys since the program objective was to study the effect of uncombined Ca and Mg.

The effect of Ca on the hot workability of selected Ni-Fe alloys is illustrated in Fig. 10. This series shows that hot cracking is most severe at about 75Ni-25Fe and that sensitivity to uncombined Ca is greatly diminished in high-Fe alloys. In the Ni-Cr and Ni-Mo systems the greatest sensitivity to cracking occurred at about 15%Cr and 10%Mo, respectively. Otherwise, they were analogous to the Ni-Fe system. The observed behavior can be explained by the microstructural information presented earlier.
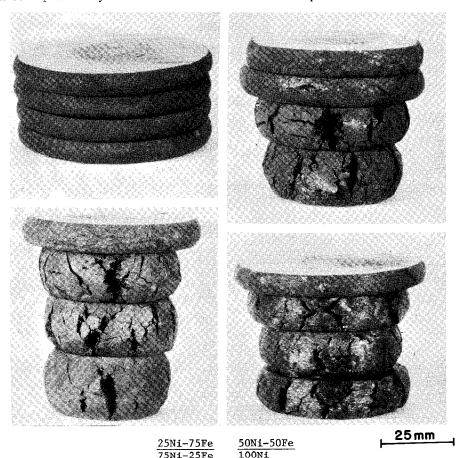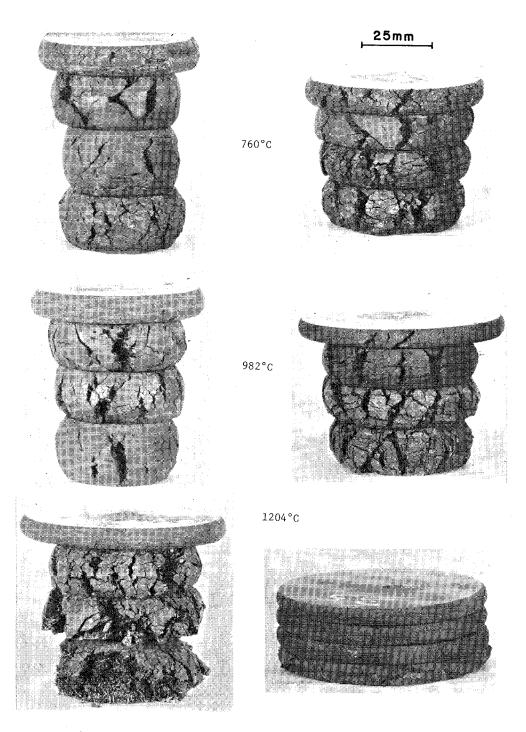

25Ni-75Fe	50Ni-50Fe
75Ni-25Fe	100Ni

FIGURE 10

EFFECT OF CALCIUM ON HOT WORKABILITY OF NICKEL-IRON ALLOYS.
AS-CAST CYLINDERS FORGED AT 982°C.

760°C

982°C

1204°C
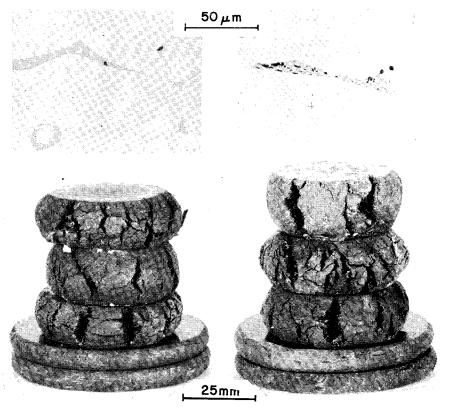
a-c) Calcium Treated   d-f) Magnesium Treated

FIGURE 11

EFFECT OF FORGING TEMPERATURE ON THE HOT WORKABILITY OF CALCIUM TREATED
Ni-25Fe ALLOYS.   AS-CAST SLUGS FORGED AT INDICATED TEMPERATURE.

The most severe cracking occurred in the alloys which have the worst combination of three factors: high volume fraction and low melting point of a continuous grain boundary film. Sensitivity is lower in high-Ni alloys when the higher melting point Ni_5Ca phase is present, and in high-Fe alloys because the volume fraction and continuity of the second phase are diminished.

The effect of forging temperature on hot workability of the Ni-25Fe alloy is shown in Fig. 11a-c. This series was representative of the behavior of all Ca-treated alloys. Note the cold cracking in all samples forged at 760°C and the gross hot shortness of samples forged at 1204°C.

It was evident from the microstructures of forged alloys in the previous series that little agglomeration or resolution occurred during the one hour soak prior to forging. However, the solid solubility data for Ca in Ni alloys (Fig. 5) suggested that prolonged soaking might dissolve or spheroidize the Ca-rich phases and thereby improve malleability. To check this, specimens were soaked for 1000 minutes (∿17 hrs.) at 1204°C and then forged. As shown in Fig. 12, there was virtually no tendency for spheroidization of the Ni_5Ca phase. Microprobe measurements showed that there was an increase in the Ca content of the matrix (maximum 0.08 w/o near the particles) but clearly dissolution is an extremely slow process at these temperatures. The prolonged soaking actually degraded the forgeability slightly. This was attributed to preferential oxidation of the Ca-rich phase. Note the internal oxidation visible in the micrograph.
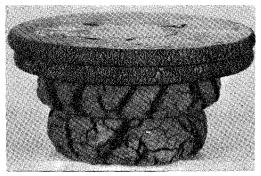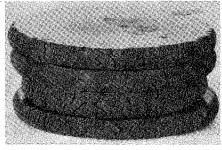

a) Soaked 60 Min at 1204°C   b) Soaked 1000 Min at 1204°C

FIGURE 12 - EFFECT OF SOAKING ON HOT WORKABILITY AND MICROSTRUCTURE OF CALCIUM TREATED Ni-9.5Cr ALLOY
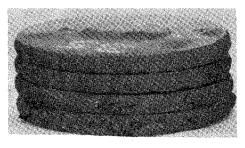
In another experiment various size castings were prepared to see if cooling rate during solidification had any influence on the formation of Ni-Ca phases. The castings ranged from 4 mm diameter chill samples to 90 mm slabs cooled in refractory brick molds. As expected the second phase particle size was considerably refined by rapid cooling but there was no effect on volume fraction or phase continuity.

The hot workability behavior of Mg-treated Ni-Fe alloys was quite different from that of Ca-treated alloys as shown in Fig. 13. In this system cracking severity increased with decreasing Ni content. Note however, that all alloys forged at 1204°C were far less sensitive to the presence of uncombined Mg. Cracking became much more severe at lower forging temperatures (Fig. 11d-f). Again the observed behavior is consistent with the prior microstructural observations. Since the Ni-Mg phases are less apt to be present as continuous grain boundary films, one would expect them to be less detrimental to malleability of Ni alloys than Ni-Ca phases. Of even greater significance is the rapid dissolution of the Ni_2Mg phase at temperatures above 1000°C. This phase was completely dissolved during a one hour soak at 1204°C in alloys containing more than about 50% Ni. The Mg solubility in Fe-rich alloys is much lower as shown in Fig. 5, hence sensitivity to hot cracking was observed. Cold cracking during forging at 760°C and 980°C could be traced directly to fracturing of the brittle Ni_2Mg particles which remained undissolved at those temperatures.

|---25mm---|

25Ni-75Fe	50Ni-50Fe
75Ni-25Fe	100Ni

FIGURE 13 - EFFECT OF MAGNESIUM ON HOT WORKABILITY OF NICKEL-IRON ALLOYS. AS-CAST CYLINDERS FORGED AT 1204°C.

Discussion

The reason for poor ductility in Ni-base alloys which contain more than critical amounts of uncombined Ca or Mg has now been established. Hot shortness in forging results from the formation of continuous low melting point intergranular films of Ni-Ca and Ni-Mg phases during ingot solidification. As these compounds are extremely brittle, Ni alloys worked at

low temperatures exhibit severe cold shortness. It had long been rec-
ognized that the malleability of Ni alloys was much more sensitive to Ca
than Mg. It now appears certain that this difference is due to the rel-
ative ease of dissolution of the Ni-Mg phases and the persistence of Ni-Ca
films during soaking. While the mechanisms are now established, the question
of translating these observations into practical guidelines remains.

In analyzing the behavior of any complex alloy system, the amount of
uncombined Ca or Mg must first be established. In most alloys all of the
residual oxygen and sulfur will be present as CaO, CaS, etc. Although Ca
and Mg form nitrides, the presence of such compounds in Ni alloys has not
been reported nor have interactions with other elements been observed.
Consequently the uncombined Ca or Mg will be that remaining after the
portion in the oxide and sulfide are accounted for. Sensitivity to crack-
ing should then correlate with the level of uncombined Mg or Ca.

The work reported here was performed largely on soft unstrengthened
ternary alloys. Certainly the inherent strength and ductility of the
matrix phase at the forging temperature will influence cracking sensi-
tivity. Some tests were performed on Ni-base alloys containing Al, Co and
various combinations of Fe, Cr and Mo. The general forging behavior of
these alloys was consistent with the preceding comments regarding the
effect of these elements on second phase composition but in each case
cracking was slightly more severe than in comparable binary alloys. Thus
one must expect that alloys with large amounts of solid solution strength-
ening elements such as Nb, W, Ta, etc. will be more sensitive to the
presence of uncombined Ca.

Because of the relative ease of dissolution of Ni-Mg phases during
soaking, it seems unlikely that the amounts of Mg which are normally added
to Ni-base alloys would cause hot cracking. Permanent damage could result
if overheating led to liquation and internal oxidation. Also hot working
followed by warm working in a critical temperature range might lead to
reprecipitation of Ni_2Mg particles and reduced ductility. However, both
problems are hypothetical and beyond the scope of the present paper.

It would appear from the foregoing discussion that the best way to avoid
forging difficulties is to add only enough Ca or Mg to deoxidize or de-
sulfurize. However, where a specific residual level is required for
mechanical or physical properties this is not possible. For such materials
a consistent recovery of the reactive element is essential if excessive
ingot losses are to be avoided. We have found that Ca and Mg recoveries of
more than 90% can be achieved by using dilute Ni-base addition alloys such
as 95Ni-5Ca or 95Ni-5Mg. While these additives do not eliminate the need
to maintain good treatment practices, they do ensure the melter consistent,
predictable residual Ca and Mg levels.

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