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DETERMINATION OF THE GASEOUS HYDROGEN DUCTILE-BRITTLE TRANSITION IN COPPER-NICKEL ALLOYS

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16. ABSTRACT

A series of copper-nickel alloys were fabricated, notched tensile specimens machined, for each alloy and the specimens tested in 34.5 MPa hydrogen and in air. A notched tensile ratio was determined for each alloy and the hydrogen environment embrittlement (HEE) determined for the alloys of 47.7 weight percent nickel to 73.5 weight percent nickel.

Stacking fault probability and stacking fault energies were determined for each alloy using the x-ray diffraction line shift and line profiles technique.

Hydrogen environment embrittlement was determined to be influenced by stacking fault energies; however, the correlation is believed to be indirect and only partially responsible for the HEE behavior of these alloys.

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INTRODUCTION

Many alloy steels and nickel-based superalloys are susceptible to a phenomenon known as hydrogen environment embrittlement (HEE) [1]. For example, some of the alloy steels become embrittled in aqueous exposure to hydrogen, while many nickel-base alloys exhibit HEE at high pressures of hydrogen [2]. This sensitivity to the hydrogen environment is manifested by a drastic reduction in their notched tensile strengths and ductility.

In the case of rocket engine turbopumps, although the nickel-base alloy blades are subjected to high stresses and extreme temperatures as well as high pressure hydrogen, a few do not succumb to HEE when the hydrogen is added. It is therefore important to know which alloys are among the few that are less impervious to hydrogen. The purpose of this investigation was to gain fundamental understanding of the hydrogen environment embrittlement mechanism.

Evaluation of the HEE susceptibility is determined by physical testing of notched tensile specimens in 34.5 MPa hydrogen and in air/helium. The notched tensile ratio hydrogen/air reveals their relative sensitivity to HEE. This unique testing procedure is inherently time consuming, expensive, and also it is relatively difficult to find qualified testing facilities. A second purpose of this investigation was to determine if an alternate method of determining HEE within an alloy system could be devised, such as correlating HEE with stacking fault energies.

HEE behavior has been explained in terms of the hydrogen being transported/ distributed by the moving dislocations [3,4]. When the stacking fault energy is low, cross slip for dislocations is very difficult; hence, moving dislocations on the slip plane will transport any hydrogen to a small region of the grain boundary as they pile up [3,5]. This will cause integrity loss in the grain boundary. Dislocations in alloys with high stacking fault energy (narrow fault widths) will easily undergo cross slip; hence, any hydrogen in the dislocation will be scattered throughout the grain with less damage to the grain boundary integrity.

OBJECTIVE

The intent of this investigation was to provide additional data that could augment the current knowledge of HEE susceptibility of certain alloy systems. The copper-nickel binary system was selected, since copper and nickel display opposite reactions to hydrogen and also have high and low stacking fault energies, respectively. The stacking fault energy determination within the copper-nickel system might provide a correlation between stacking fault energy and HEE. If the transition in stacking fault energy occurred in the same region as the change in hydrogen susceptibility, then a relationship could be surmised.

The copper-nickel alloy system is known to contain a hydrogen-sensitive transition region (i.e., a band of copper-nickel compositions susceptible to hydrogen damage). The stacking fault energies of various copper-nickel samples have been evaluated with respect to composition for the possible existence of a wide variation in stacking fault energy in the transition region. The existence of a wide variation in stacking fault energy in the transition may allow the prediction of hydrogen susceptibility of other alloys without expensive hydrogen testing.

DISCUSSION

A. Alloy Preparation

Alloys were prepared by vacuum melting selected amounts of copper and nickel pellets (Table 1). Each 2.5 in. diameter alloy bar was homogenized at 2000°F and cross rolled until each ingot was a 3.0 in. wide plate, followed by longitudinal rolling until a 1.25 in. thick plate was achieved. The plate was then water cooled to room temperature, then cold rolled to a final thickness of 0.625 in. A recrystallization study was performed to determine the optimum temperature for obtaining a fine equiaxed grain. All alloys were then recrystallized at 1400°F (760°C) for 2 hours.

B. Hydrogen Environment Tests

Suitable notched tensile specimens were machined from each plate for hydrogen environment (HEE) tests (Fig. 1). All high pressure hydrogen tests were conducted by Pratt and Whitney Aircraft, West Palm Beach, Florida (Table 2). Figure 2 shows the relationship of the notched tensile ratio (hydrogen/air) to the alloy composition.

C. X-Ray Diffraction

The analysis of changes in profiles and position of the diffraction lines in the x-ray powder patterns is a valuable technique for the investigation of the structure and properties of crystalline materials. In particular, the effect of deformation on the powder patterns of metals and alloys has been studied extensively over the past two decades.

Broadening of the peak profile is usually produced by a reduction in the size of the coherently diffracting domains (crystallite size), by faulting on the certain (hkl) planes, and by microstrains within the coherently diffracting domains [6,7]. The changes in peak position may be due to residual stress in bulk specimens, to faulting, and to lattice parameter changes produced by dislocations and segregation of solute atoms [8,9,10].

The broadening produced by small crystallite sizes and faulting is independent of the order of reflection; whereas, the strain broadening depends on the order of reflection. The peak shifts produced by faulting and residual stresses vary with the crystallographic orientation of the reflecting planes.

In addition to the broadening and peak shifts produced by the condition of the sample, the geometry of the x-ray diffractomer also affects the shape and position of the powder pattern peaks.

Powders of Cu-Ni alloys were prepared with grains $\leq 44\mu$ in diameter by filing at room temperature. Care was taken to avoid heating of the bulk material. A portion of powder was annealed at 815.5°C in an Argon environment for 2 hours for the study of geometric broadening of the x-ray diffraction lines. Satisfactory samples were prepared by hand-pressing the powder into a suitable holder using a solution of "Duco" cement in acetone as a binder.

Monochromatic Cu $K\alpha$ radiation with nickel filter, and a standard commercial diffractometer were used with a flat specimen holder. Data were collected through a Data Control and Processor, stored on a disk, and calculated using a computer program which corrected for the background intensity, the Lorentz-polarization factor, atomic scattering factor, and subtracted the $K\alpha$ 2 intensity by the Rachinger method [11]. The profiles were Fourier analyzed using a computer program and corrected for instrument broadening. The Warren-Averbach analysis was used to calculate the microstrain [12].

The stacking-fault energy, γ, is the surface energy per unit area necessary to produce the fault. When γ is low, the separation between the partial dislocation will be large and the fault will occur frequently; i.e., the stacking-fault probability will be high. The stacking-fault energy can be expressed as [13]:

$$\gamma = \frac{k_{111} W_o G_{(111)}\ a_o}{\pi\sqrt{3}} \ \frac{<\varepsilon_{50}\ {}^2\ 111\ A^{-0.37}}{\alpha} \tag{1}$$

here $K_{111}W_o$ = 6.6 = proportionality constant

G_{111} = Shear modulus in the (111) fault plane

A = Zener elastic anisotropy = 2 $C_{44}/(C_{11} - C_{12})$ [14]

a_o = lattice constant .

The mean microstrain, $<\varepsilon 50^2>_{111}$, which can be calculated from the Fourier coefficients of the line profiles is averaged over a distance of 50 Å in the (111) direction.

The stacking fault probability, α, which corresponds to a stacking fault on the average once every $1/\alpha$ layers in the stacking of {111} layers is related to the change in peak separation of adjacent peaks between the filed and annealed peak profiles. The stacking fault probability may be calculated from equation (2).

$$\delta(\Delta 2\theta^\circ)_{hkl-h'k'l'} = H_{hkl-h'l'l'}\alpha \tag{2}$$

where $H_{hkl-h'k'l'}$ depends only on the reflecting lattice planes [10].

RESULTS

A. Hydrogen Testing

Hydrogen Environment Embrittlement (HEE) is usually determined by performing notched tensile tests in 34MPa hydrogen gas and in air. The ratio of the notched ultimate strengths (hydrogen to air) represents the apparent susceptibility to HEE (Fig. 2). The HEE susceptibility transition is readily seen above 50 weight percent nickel. This rapid loss of strength attributed to HEE has never been satisfactorily explained and is always determined by actual mechanical tests in the appropriate environments.

B. X-Ray Diffraction

A series of copper-nickel alloys were processed into cold worked and annealed powders. Since stacking fault probability (α) and stacking fault energy (γ) are directly related to diffraction line shifts and line profiles between cold worked and annealed powders, a series of x-ray diffraction measurements were obtained on each copper nickel alloy (Tables 3, 4, 5, 6). A graph of the stacking fault probability versus composition is shown in Figure 3. The present data and that obtained from literature each show a maximum at about 50 weight percent nickel corresponding to the transition zone indicated in the data from mechanical testing in high pressure hydrogen.

The stacking fault energy results shown in Figure 4 were calculated using the stacking fault probability and the microstrain obtained from diffraction line profiles. The stacking fault energies do not change appreciably with increasing nickel content; therefore, a direct correlation between stacking fault energy and composition may not be feasible using the current technique [13,16].

SUMMARY

Hydrogen Environment Embrittlement (HEE) has been determined to be influenced by stacking fault energies; however, the correlation must be indirect and only partially responsible for the HEE behavior of many alloys. We have shown that the stacking fault probability suggests that the transition zone is related to HEE onset, but stacking fault energies do not markedly change with composition in the range of alloys under investigation. It is evident that a significant increase in precision of the x-ray diffraction measurements may not be sufficient to produce a direct correlation between stacking fault energy and hydrogen environment embrittlement.

REFERENCES

1. McPherson, W. B.: Personal Communication.

2. Parr, R. A.; Alter, W. S.; Johnston, M. H.; and Strizak, J. P.: NASA TM-86464, 1984.

3. Thompson, A. Q.: Hydrogen in Metals. Eds. I. M. Bernstein and A. W. Thompson, ASM, Metals Park, Ohio, 1984, p. 91.

4. West, A. J. and Louthan, Jr., M. R.: Met Trans A 10A, 1979, p. 1675.

5. Odegard, B. C.; Brooks, J. A.; and West, A. J.: Effect of Hydrogen on Behavior of Materials. Eds. I. M. Bernstein and A. W. Thompson, AIME, New York, 1984, p. 116.

6. Warren, B. E.: Progress in Metal Physics, 8, Pergamon Press, New York, 1952, p. 147.

7. Wager, C. N. J.: Local Atomic Arrangement Studied by X-Ray Diffraction, Eds. J. B. Cohen and J. E. Hilliad, Gordan and Breach, New York, Chap. 7.

8. Wager, C. N. J.; Tetelman, A. S.; and Otte, H. M.: J. Appl. Phys., 33, 1962, p. 3080.

9. Adler, R. P. I. and Wager, C. N. J.: J. Appl. Phys., 33, 1965, p. 3451.

10. Wager, C. N. J. and Hoelion, J. C.: J. Appl. Phys., 33, 1962, p. 4351.

11. Rachinger, J. Sci. Instrum., 25, 1948, p. 254.

12. Warren, B. E.: X-Ray Diffraction, Addison-Wesley, 1969, Chap. 13.

13. Reed, R. P. and Schramm, R. E.: J. Appl. Phys., 45, 1984, p. 4505.

14. Epstein, S. G. and Carlson, O. N.: Acta Met., 13, 1960, p. 487.

15. OH, T. K.: M.S. Thesis, University of Alabama-Huntsville, 1984.

16. Davis, J. H. and OH, T. K.: NAS8-33811 Final Report, University of Alabama-Huntsville, 1984.

TABLE 1. ALLOY COMPOSITIONS

Sample	Copper (wt. %)	Nickel (wt. %)
1	52.3	47.7
2	43.7	56.3
3	38.3	61.7
4	34.4	65.6
5	31.2	68.8
6	26.5	73.5

TABLE 2. NOTCHED TENSILE RATIOS OF COPPER-NICKEL ALLOYS

Composition wt. % Ni	Ultimate Strength (MPa)		Notched Ratio H_2/Air
	H_2*	Air	
47.7	512.3	533.3	0.96
56.3	426.5	576.7	0.74
61.7	402.4	583.6	0.69
65.6	369.3	602.2	0.61
68.8	351.7	608.7	0.58
73.5	313.2	601.5	0.52

* 34.5 MPa Hydrogen - Room Temperature

TABLE 3. SHEAR MODULUS AND ZENER ELASTIC ANISOTROPY [14]

Alloy (wt. % Ni)	C_{11} (10^{12} dyne/cm^2)	C_{12}	C_{44}	G_{111} (10^{11} dyne/cm^2)	A
47.7	2.08	1.40	0.98	5.53	3.06
56.3	2.12	1.43	1.03	5.73	2.99
61.7	2.16	1.44	1.06	5.93	2.94
65.6	2.20	1.45	1.08	6.10	2.88
68.6	2.22	1.46	1.10	6.20	2.89
73.5	2.25	1.47	1.12	6.22	2.87

TABLE 4. LATTICE PARAMETER DEPENDENCE ON COLD WORK

ALLOY (wt. % Ni)	$a_{C.W.}$ # Å	a_{an} # Å	$\Delta a(a_{C.W.}-a_{an})$ Å
47.7	3.5718	3.5731	-0.0013
56.3	3.5627	3.5647	-0.0020
61.7	3.5586	3.5605	-0.0019
65.6	3.5552	3.5578	-0.0026
68.8	3.5626	3.5541	-0.0015
73.5	3.5479	3.5499	-0.0020

Extropolation by least square fitting of five reflections

TABLE 5. STACKING-FAULT PROBABILITY

ALLOY (wt. % Ni)	$\delta(\Delta 2\theta)$ (C.W.-An) # (θ_{222} $-\theta_{200}$) (DEGREES)	$\alpha \times 10^3$	$\alpha^* \times 10^3$
47.7	0.069 ± 0.005	10.07	8.38
56.3	0.061 ± 0.003	8.90	6.27
61.7	0.048 ± 0.002	7.01	4.37
65.6	0.046 ± 0.006	6.73	3.37
68.8	0.052 ± 0.004	7.57	5.49
73.5	0.048 ± 0.004	6.97	4.23

Error limit present $\pm\sigma$ from 5∿9 independent measurements

* Corrected for lattice parameter change

TABLE 6. MICROSTRAIN AND STACKING-FAULT ENERGY [15]

ALLOY (wt. % Ni)	$\alpha^* \times 10^3$	$\langle\varepsilon_{50}^2\rangle \times 10^6$	$\frac{\langle\varepsilon_{50}^2\rangle}{\alpha^*}$	γ (erg/cm^2)
47.7	8.32	3.84	4.62	7.3
56.3	6.27	1.41	2.25	3.7
61.7	4.37	1.26	2.88	5.0
65.6	3.37	1.53	4.54	8.1
68.8	5.49	8.48	15.4	27.8
73.5	4.23	4.15	9.81	18.1

* Corrected for Lattice Parameter Change

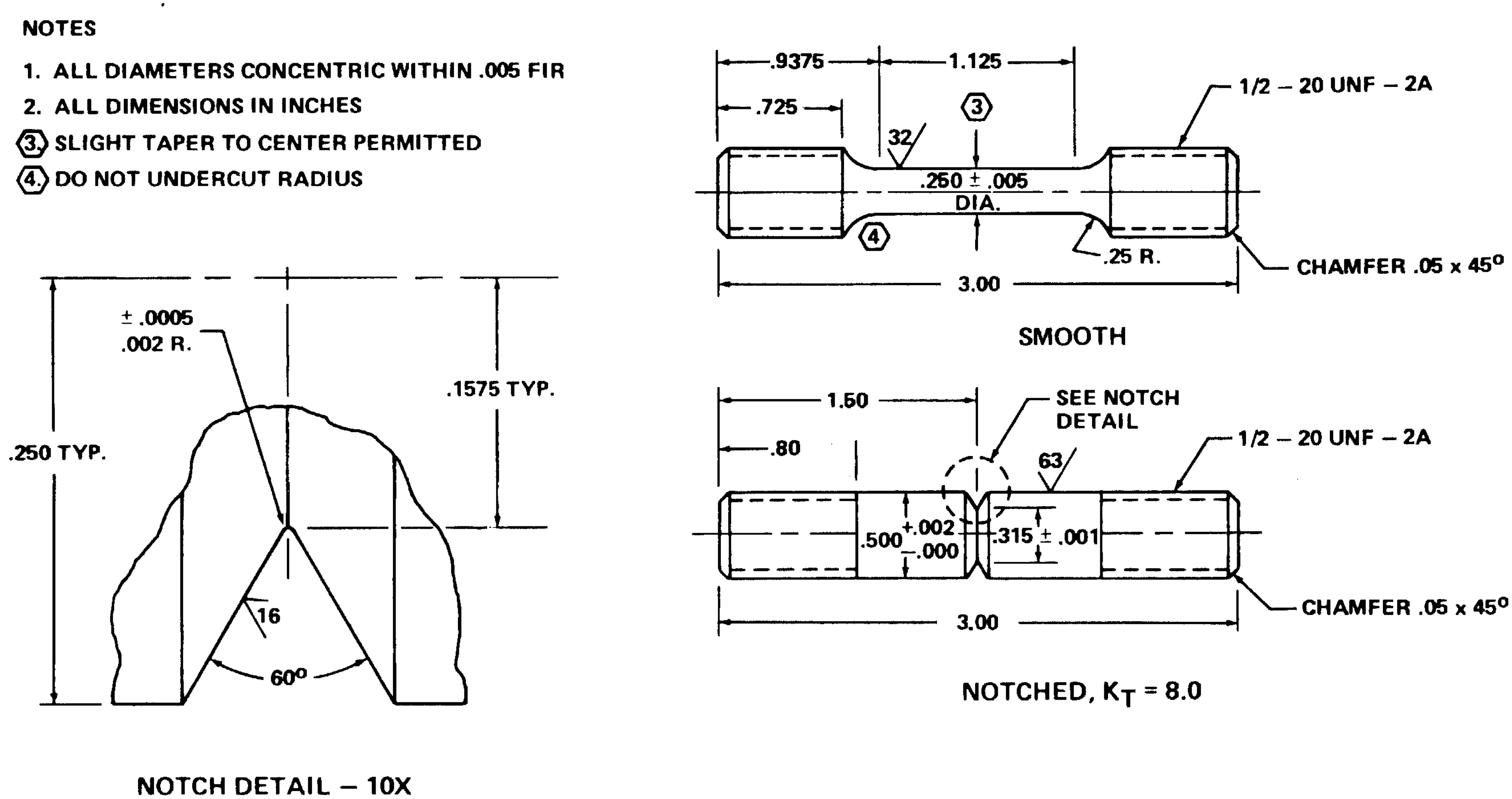

Figure 1. Notched tensile specimen.

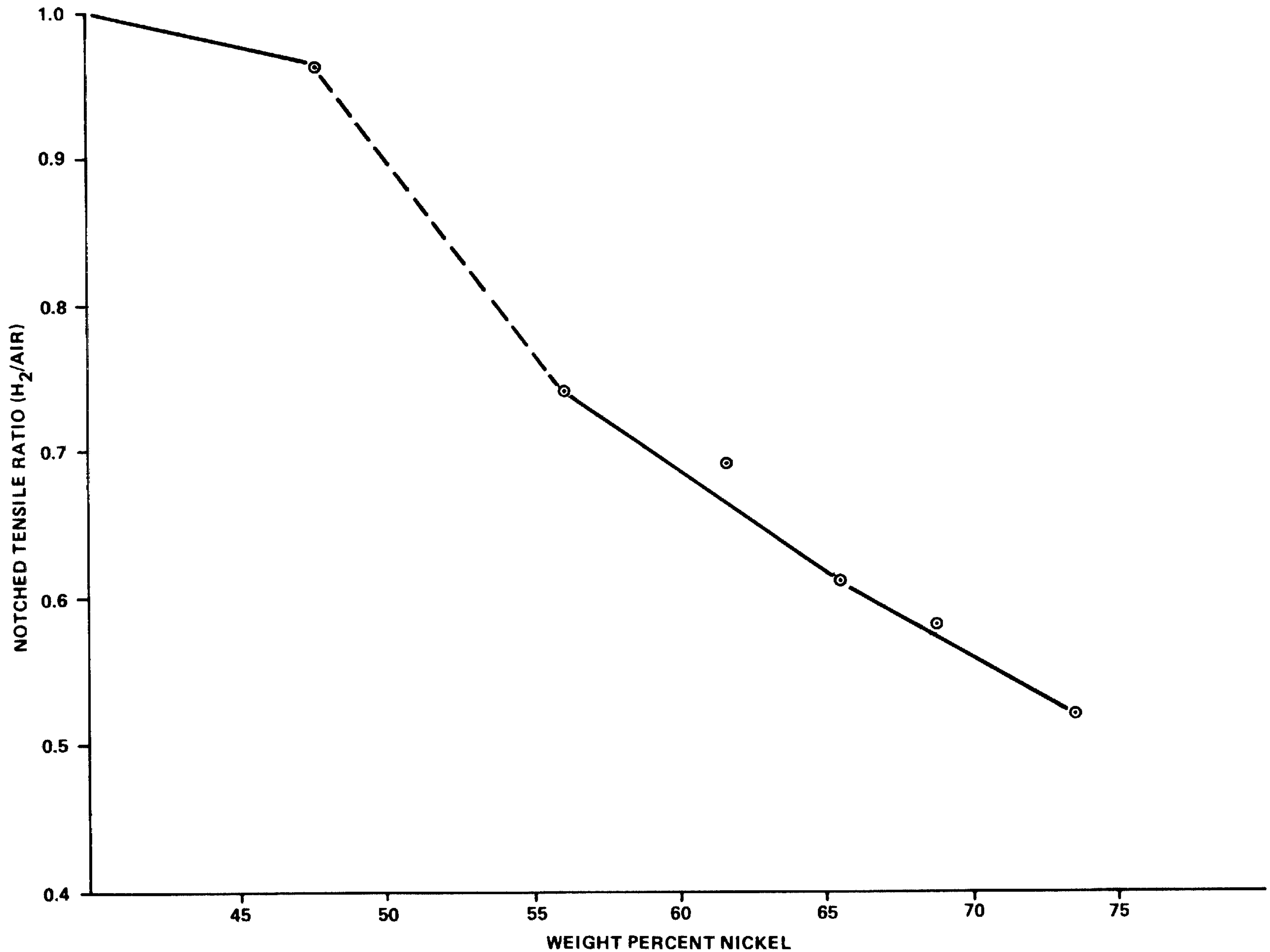

Figure 2. Notched tensile ratio versus weight percent nickel in copper-nickel alloys

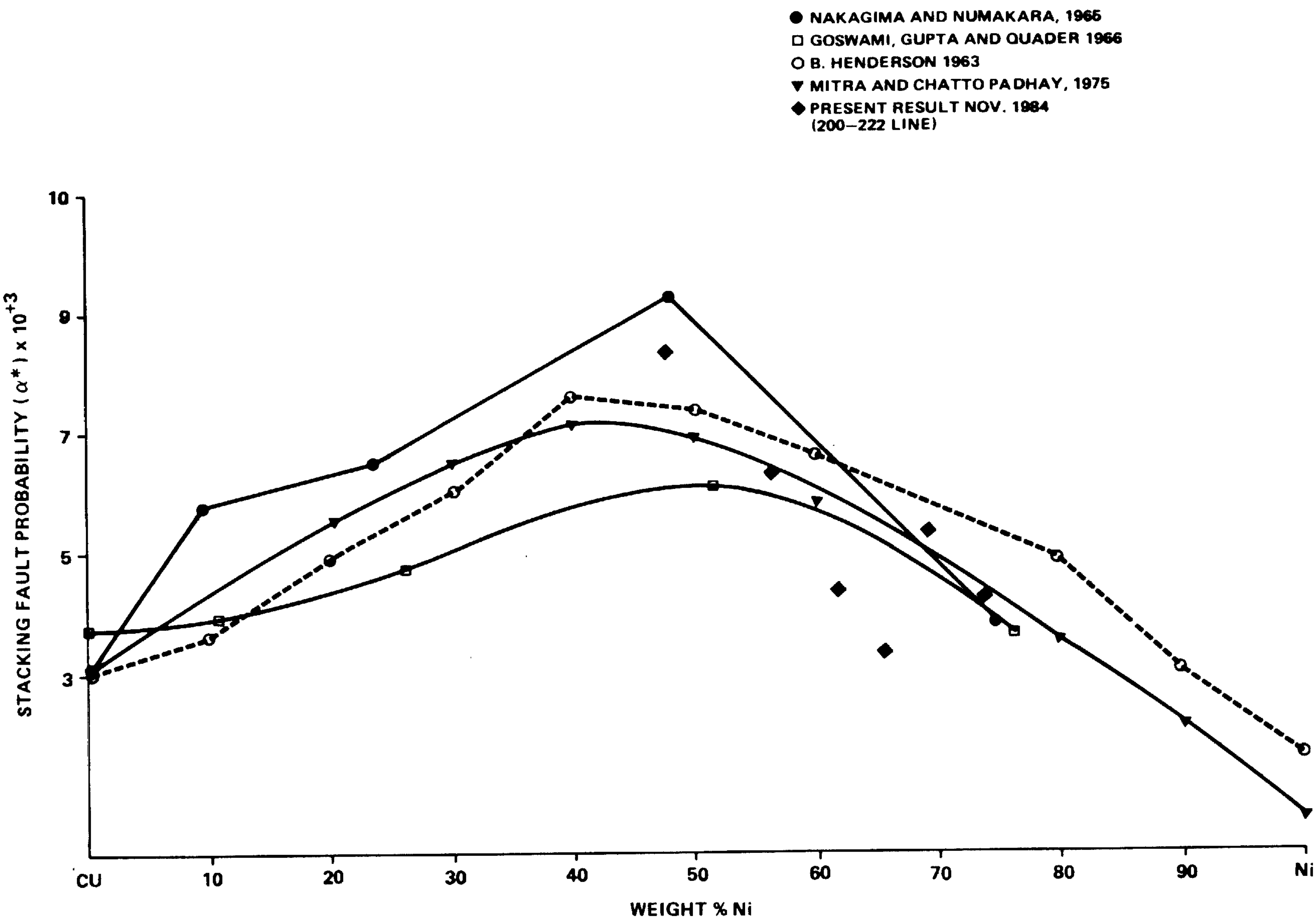

Figure 3. Stacking fault probability versus weight percent nickel.

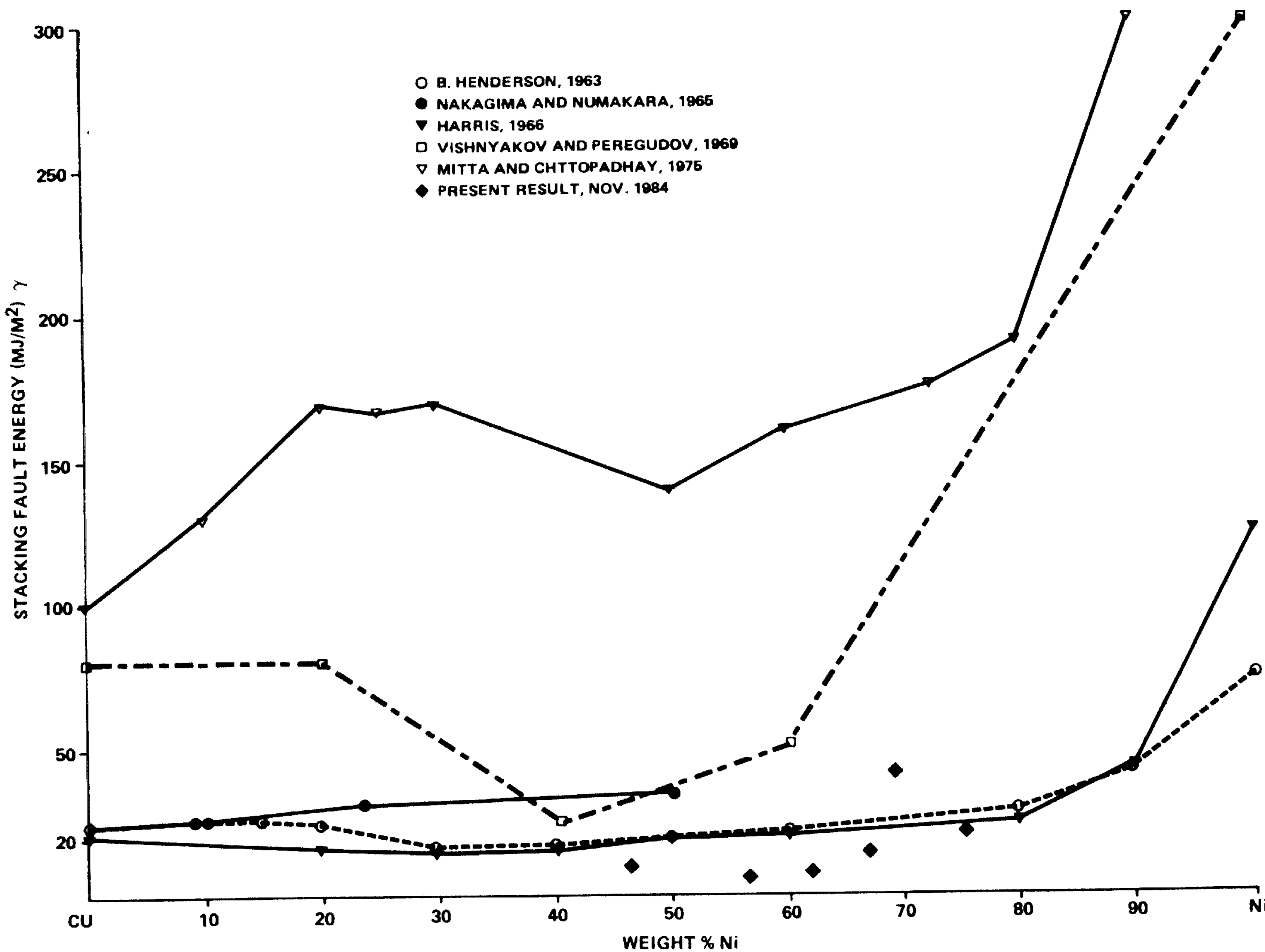

Figure 4. Stacking fault energy versus weight percent nickel.

APPROVAL

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The information in this report has been reviewed for technical content. Review of any information concerning Department of Defense or nuclear energy activities or programs has been made by the MSFC Security Classification Officer. This report, in its entirety, has been determined to be unclassified.

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