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THE ROLE OF DILUTE BINARY TRANSITION ELEMENTS ON THE RECRYSTALLIZATION OF NICKEL

TECHNICAL REPORT NO. WAL TR 830.3/7

ERNEST P. ABRAHAMSON, II

DATE OF ISSUE - NOVEMBER 1961

OMS CODE 5010.11.8050051
GENERAL MATERIALS PROBLEMS, RESEARCH AND INVESTIGATION
D/A PROJECT 5893-32-001

WATERTOWN ARSENAL
WATERTOWN 72, MASS.
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ABSTRACT

The effect of transition element binary solid solution additions upon the recrystallization temperature of nickel has been investigated. All additions raised the recrystallization temperature. Both the rate of change of recrystallization temperature with atomic percent solute and the limit of initial linearity are found to correlate with the free atom ground state outer electron configuration of the solute element.

ERNEST P. ABRAHAMSON, II
Supervisory Physical Metallurgist

APPROVED:

J. F. SULLIVAN
Director
Watertown Arsenal Laboratories
INTRODUCTION

The work of Abrahamson, et al,1-7 on dilute binary solid solution alloys indicated a correlation between the free atom ground state electron configuration of the solute and both the brittle-ductile transition and recrystallization temperature. Further, it has been shown3,4 that the limit of initial linearity may also be correlated with the solute electron configuration. Since previous studies have dealt with body-centered-cubic and hexagonal-close-packed solvents, this study was made to note what effect, if any, the face-centered-cubic base structure might have.

Olsen8 has studied the effect of some trace elements upon the recrystallization of nickel. He included only Ti, Zr, W, Mn and Co of the transition elements. The differences in change of recrystallization temperature were attributed to the solute atom size and its solubility in nickel.

PROCEDURE

All alloys were made using 99.9+ percent nickel with 0.003 C, 0.015 Fe, 0.007 O, and 0.0007 H. The solute elements were 99.9+ percent pure. According to the published binary phase diagrams9 and metallographic examinations at 750X, all alloys used were in solid solution.

The alloys were arc melted and remelted four times in the form of cubic 200-gram buttons under an argon atmosphere. They were then hot forged at 800 C to 0.750-inch diameter, machined to 0.60-inch, vacuum annealed for one hour at 700 C, swaged to 0.40-inch diameter, and annealed at 700 C for one hour in vacuum. The grain size was checked and found to be 77 ± 20 grains per sq mm. The specimens were then swaged to 0.187-inch diameter rod, yielding 76 ± 1 percent cold work. All alloys were then chemically analyzed for the solute addition. The interstitial contents remained the same as the values of the starting material when checked on random alloy specimens.

The swaged rod was cut into 8.25-inch lengths and heat treated in a gradient furnace for one hour. The gradient was maintained at 250 to 850 C over an 8-inch length, and recorded by 12 thermocouples. Control was ± 3 C, accomplished at the hot end.

The recrystallization was determined metallographically over the entire specimen. The criterion chosen was that point on the specimen showing the first recrystallized grain at a constant magnification, 200X. Specimens were repeated, and the agreement was found to be generally ± 3 C.
RESULTS

Seven different pure nickel specimens were tested, and the recrystallization temperature was found to be $355 \pm 3^\circ$ C. Figures 1 through 3 show the effect of the transition elements on the recrystallization of nickel. All elements immediately raise the recrystallization temperature.

If one considers the slope of the curves in Figures 1 through 3, a definite periodicity can be noted. Further, the limit of initial linearity is also periodic. A plot of these two parameters versus the free atom ground state outer d shell electron configuration demonstrates this periodicity, c.f. Figures 4 and 5.

DISCUSSION

As in previous systematic studies, a correlation is noted between the change in recrystallization temperature with solute, and the number of outer d shell electrons in the solute. All of the curves studied have been in the form of upright or inverse V's with the apex of the $s^2$ electron curve consistently occurring at one d electron more than the solvent.

On this basis, nickel would be expected to have an apex in the $s^2$ curve at $d^9$. Unfortunately there are no elements which exist with configurations of $d^9$ $s^2$ or $d^{10}$ $s^2$ to check this. However, the positioning of the $s^0$ curve strongly suggests that the apex occurs at $d^9$.

When one considers the difference in recrystallization parameter and purity of the base metal used by Olsen, the comparison of AT's is quite good. In general the data of Olsen is somewhat higher than that of this study, but the relative trend of the slope values is in agreement with the correlation. In considering Olsen's suggestion that the differences in recrystallization temperature can be attributed to the solute atom size and its solubility, a careful check of all of the systems studied, c.f. table, does not show any direct relationship.

It is felt that both atomic size and solubility limit can be considered to be functions of electronic make-up and the interaction of electron band structures in alloys. Thus rough correlation with these parameters would be expected. However, it appears that direct correlation with the electronic structure of the individual atoms yields more consistent results.

The correlation curve for the limit of linearity versus the number of solute outer d shell electrons is implied to be in the form of an inverse V, with an apex at $d^9$. This assumption is based on the same reasoning as for the slope correlation curve.

These results tend to suggest that the solvent lattice structure does not effect the electron configuration correlation. There yet remains the
combination of results from the results on body-centered-cubic, hexagonal-close-packed, and the face-centered-cubic solvent material to attempt to yield a workable theory and set of equations. This will be considered in detail in a later report.

<table>
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<tr>
<th>System</th>
<th>Goldschmidt Deviation</th>
<th>Solubility Limit at. % deg C/at. %</th>
<th>Solute Percent</th>
<th>Room Temp</th>
<th>Initial Slope</th>
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* No Test Data
** Unknown

CONCLUSION

1. All transition elements studied raised the recrystallization temperature of nickel.

2. A correlation is noted between the slope of the recrystallization temperature versus atomic percent solute curve and the limit of linearity and the number of outer d shell electrons attributed to the solute atom in the ground state. The curve is in the form of a V with an apex at d⁹.
ACKNOWLEDGMENTS

The author wishes to thank the Watertown Arsenal Metallurgical Services, Analytical Chemistry and Fundamental Research Branches for their assistance. He further wishes to thank Mr. D. Tracy for his assistance and Mr. J. A. Alexander and Dr. F. Rhines for their helpful discussions.
Figure 1: Recrystallization temperature versus atomic percent solute for the first transition series.

- Ti
- Cr
- Mn
- Fe
- Co
RECRYSTALLIZATION TEMPERATURE VERSUS ATOMIC PERCENT SOLUTE FOR THE SECOND TRANSITION SERIES.

- Figure 2
Recrystallization temperature versus atomic percent solute for the third transition series.

Figure 3
RATE OF CHANGE OF RECRYSTALLIZATION TEMPERATURE WITH ATOMIC PERCENT SOLUTE VS GROUND STATE OUTER ELECTRON CONFIGURATION OF SOLUTE.
ATOMIC PERCENT SOLUTE AT BREAK FROM LINEARITY
VERSUS GROUND STATE OUTER ELECTRON CONFIGURATION OF SOLUTE.

FIGURE 5
REFERENCES


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