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THE ROLE OF DILUTE BINARY TRANSITION ELEMENT
ADDITIONS ON THE RECRYSTALLIZATION OF VANADIUM

TECHNICAL REPORT NO. WAL TR 830.3/3

BY

ERNEST P. ABRAHAMSON, II

JULY 1961

OMS CODE 5010.11.8050051
GENERAL MATERIALS PROBLEMS, RESEARCH AND INVESTIGATION

WATERTOWN ARSENAL
WATERTOWN 72, MASS.

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Recrystallization
Transition elements
Vanadium

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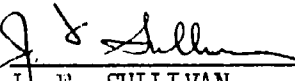
THE ROLE OF DILUTE BINARY TRANSITION ELEMENT ADDITIONS
ON THE RECRYSTALLIZATION OF VANADIUM

ABSTRACT

The effect of transition element binary solid solution additions upon the recrystallization temperature of vanadium has been investigated. Cr, Fe, Co, Ni, Mo, Ru, Rh, Os and Ir lower the recrystallization temperature, while Ti, Mn, Zr, Nb, Pd, Hf, Ta, W, Re and Pt raise it. The majority of elements have their greatest effect in less than 0.15 atomic percent. 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
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APPROVED:


J. F. SULLIVAN
Director
Watertown Arsenal Laboratories

INTRODUCTION

The work of Abrahamson and Grant¹ and Abrahamson and Blakeney² has shown that the solute's electron configuration appears to be a prime determinant of both brittle-to-ductile transition and recrystallization temperature in dilute binary alloys. It has also been shown by Abrahamson³ that the limit of linearity, i.e., the limit of initial linear change of recrystallization temperature with atomic percent solute, is also a function of the electron configuration of the solute in iron base alloys.

Because of the systematic nature of the solute electron configuration correlation, it is to be expected that some systematic variation might be observed upon changing the solvent. Thus, this study of recrystallization in vanadium-base alloys is the first of a series aimed at defining the role played by the electron configuration of solute in determining the recrystallization characteristics of dilute transitional alloys.

PROCEDURE

All alloys were made using 99.8 percent vanadium containing 0.011 C, 0.024 N, 0.08 O, 0.006 H, 0.035 Ta, and 0.01 Fe. All solute elements were 99.9+ percent pure. According to the published phase diagrams⁴ and metallographic examination at 750X, all alloys used were solid solutions.

The alloys were arc melted six times and cast into cubic 400-g ingots under an argon atmosphere. They were then hot forged at 1200 C to 0.6 inch diameter, annealed for three hours at 1000 C under argon and furnace cooled. The specimens were then machined to 0.400 inch diameter. Grain size was checked and found to remain essentially constant at 140 grains $\pm$ 30 per sq mm. The specimens were then swaged to 0.187 inch diameter, yielding 46 $\pm$ 1 percent cold work. The alloys were all analyzed chemically or spectrographically or both. In all cases the interstitial content remained within 10 percent of the values of the starting material, and the tungsten pickup was limited to 0.006 to 0.007 wt percent.

The swaged rod was cut into 8-1/4-inch lengths and heat treated in a gradient furnace for one hour. The gradient was 600 to 1100 C over an 8-inch length, recorded by 12 thermocouples and controlled to $\pm$ 3 C at the hot end.

The recrystallization temperature was determined metallographically at 200X as that temperature at which the first recrystallized grain appears. Specimens were rechecked and the agreement was generally found to be $\pm$ 2 C.

RESULTS

Eight different pure vanadium specimens were tested, and the recrystallization temperature was found to be 860 C. Figures 1 through 3 show the effect of the three transition series on the recrystallization of vanadium. The elements Cr, Fe, Co, Ni, Mo, Ru, Rh, Os, and Ir lower the recrystallization temperature, while Ti, Mn, Zr, Nb, Pd, Hf, Ta, W, Re, and Pt raise it. All but three of the additives result in a reduction of absolute slope at additions of less than 0.15 atomic percent solute (less than solubility limit). Three solutes, Ti, Zr, Hf, yield slope increases at similarly low solute concentration. Such increases in slope were not noted in the iron or chromium-base systems.^{1,2,3}

The iron recrystallization studies indicated that all the transition elements immediately raised the recrystallization temperature. In the present study one-half of the elements immediately raised it.

If one considers the absolute slope of these data, Figures 1 through 3, a definite periodicity can be noted. Further, the solute composition at which the break in the curve occurs, i.e., 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, cf. Figures 4 and 5.

DISCUSSION

As shown previously on iron-base recrystallization^{2,3} and chromium-base brittle-to-ductile transition studies¹, an electron configuration correlation is present. It has previously been postulated by the author that these property changes are a prime function of the electron configuration of the elements concerned. The data on vanadium-base alloys support this postulation.

The recrystallization temperatures and the limit of initial linearity are functions of the free atom ground state outer d and s electrons of the solute. Those elements with the same outer electron configuration have similar rates of temperature changes or limits of linearity. Solute elements having like numbers of s shell electrons lie on the same curves. The curves for s = 0, 1 and 2 electrons are parallel.

For solute atoms having a like number of d shell electrons, the fewer outer s shell electrons, the greater the magnitude of absolute rate of recrystallization temperature change.

The vanadium-base correlation differs in shape from that observed in iron in that it is in the form of an inverse "V". However, the relative positions of the s = 0, 1 and 2 curves remain the same. The apex in the s = 2 curve is found at the element tungsten whose d shell configuration is one more than that of the solvent.

The Ti, Zr, and Hf alloys are the first to show a lesser effect on recrystallization temperatures at the low concentrations than at higher concentration and this is worthy of note.

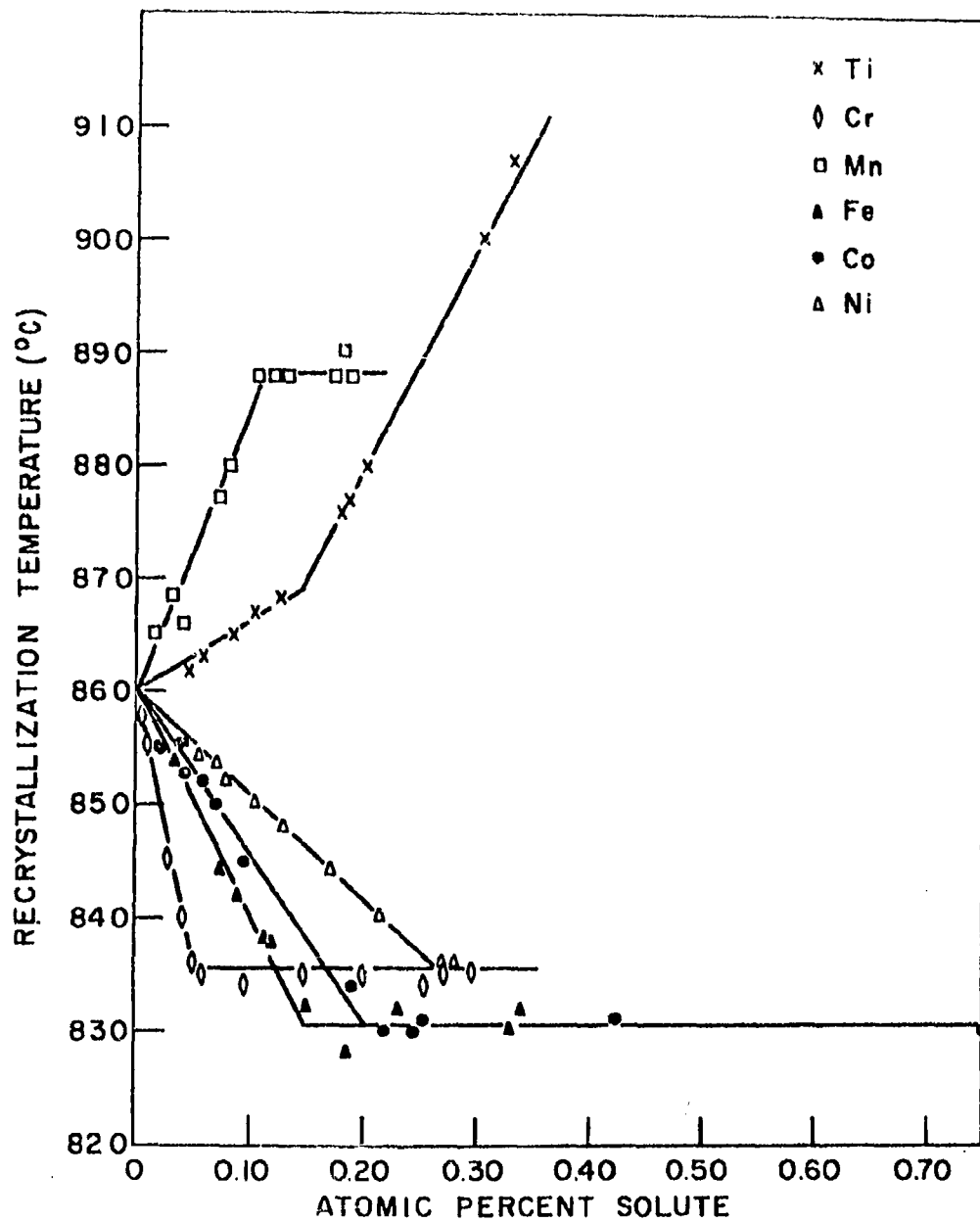
CONCLUSIONS

1. The elements Ti, Mn, Zr, Nb, Pd, Hf, Ta, W, Re, and Pt raised and Cr, Fe, Co, Ni, Mo, Ru, Rh, Os, and Ir lowered the recrystallization temperature of vanadium.
2. All of the elements exhibit a limit of linearity at less than the solid solubility limit.
3. A correlation exists when the number of outer s shell electrons in the solute is constant, such that both the logarithm of the absolute rate of change of recrystallization temperature with atomic percent solute, and limit of linearity, are linear functions of the number of d shell electrons of the solute. The curves for additives having 0, 1 and 2 outer s electrons are parallel. A maximum occurs in the $s = 2$ curve with 4 d shell electrons.
4. Atoms with the same outer electron configurations exhibit similar effects.

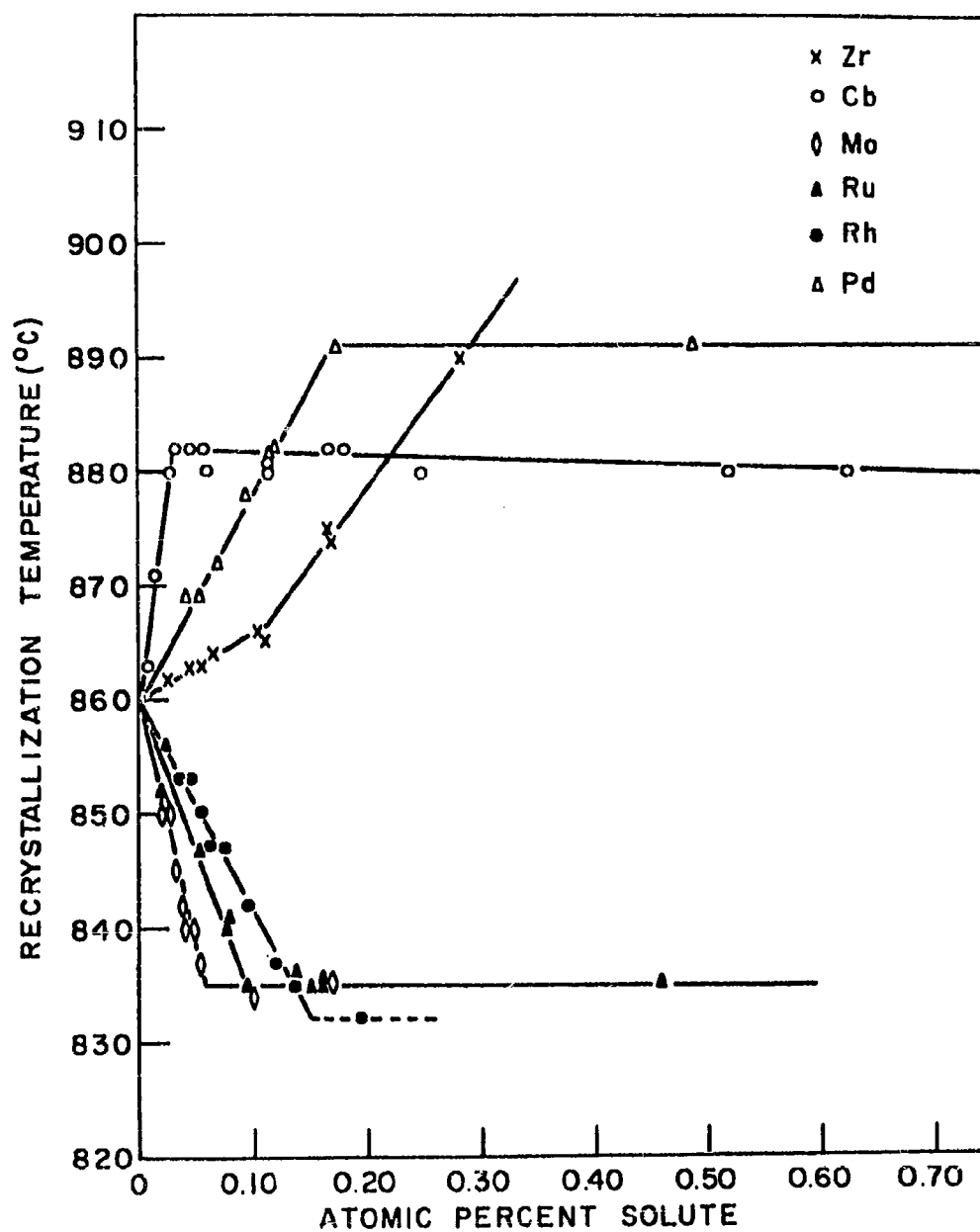
ACKNOWLEDGMENTS

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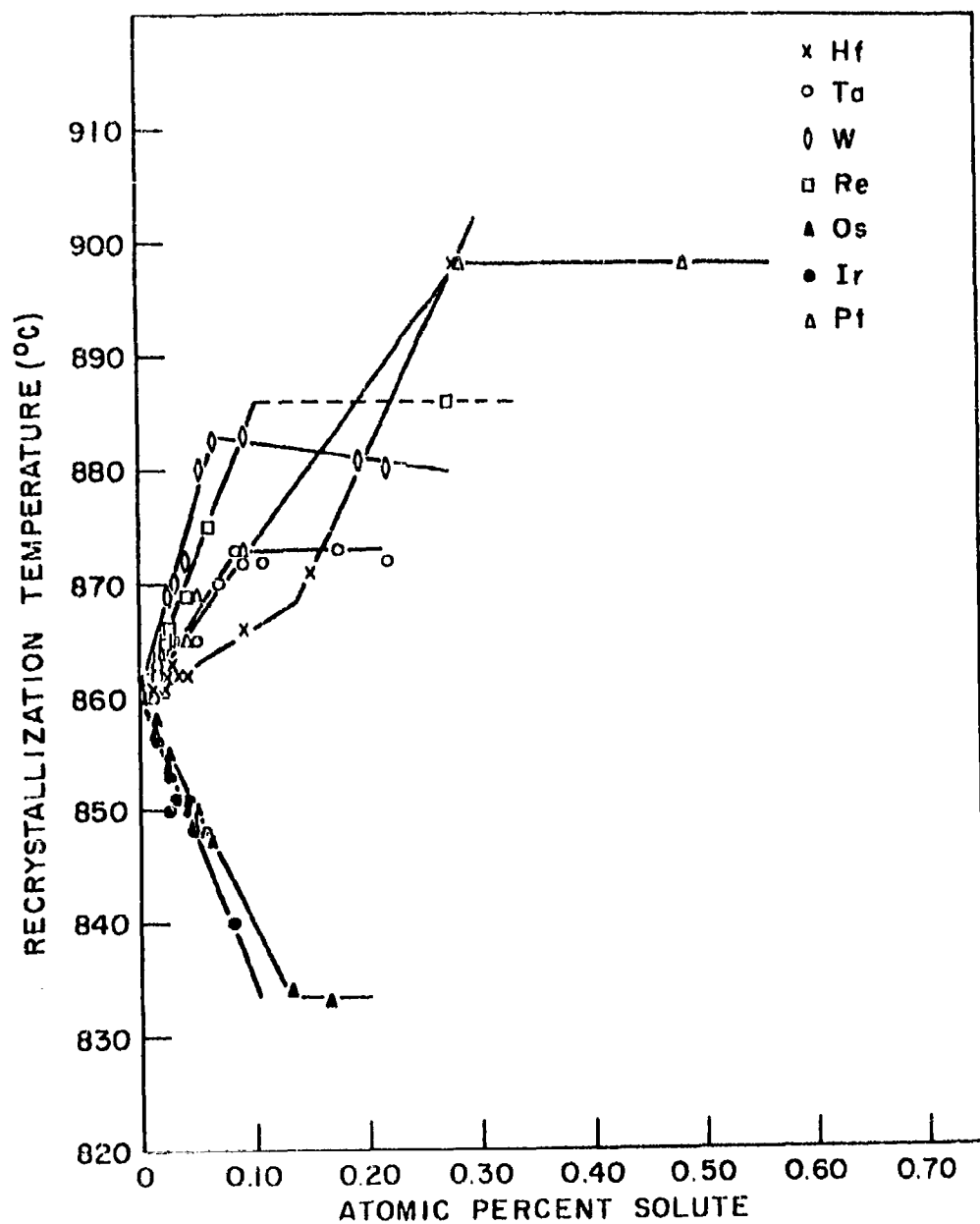
He further wishes to thank Mr. J. A. Alexander and Dr. F. Rhines for their many helpful discussions of the problem.



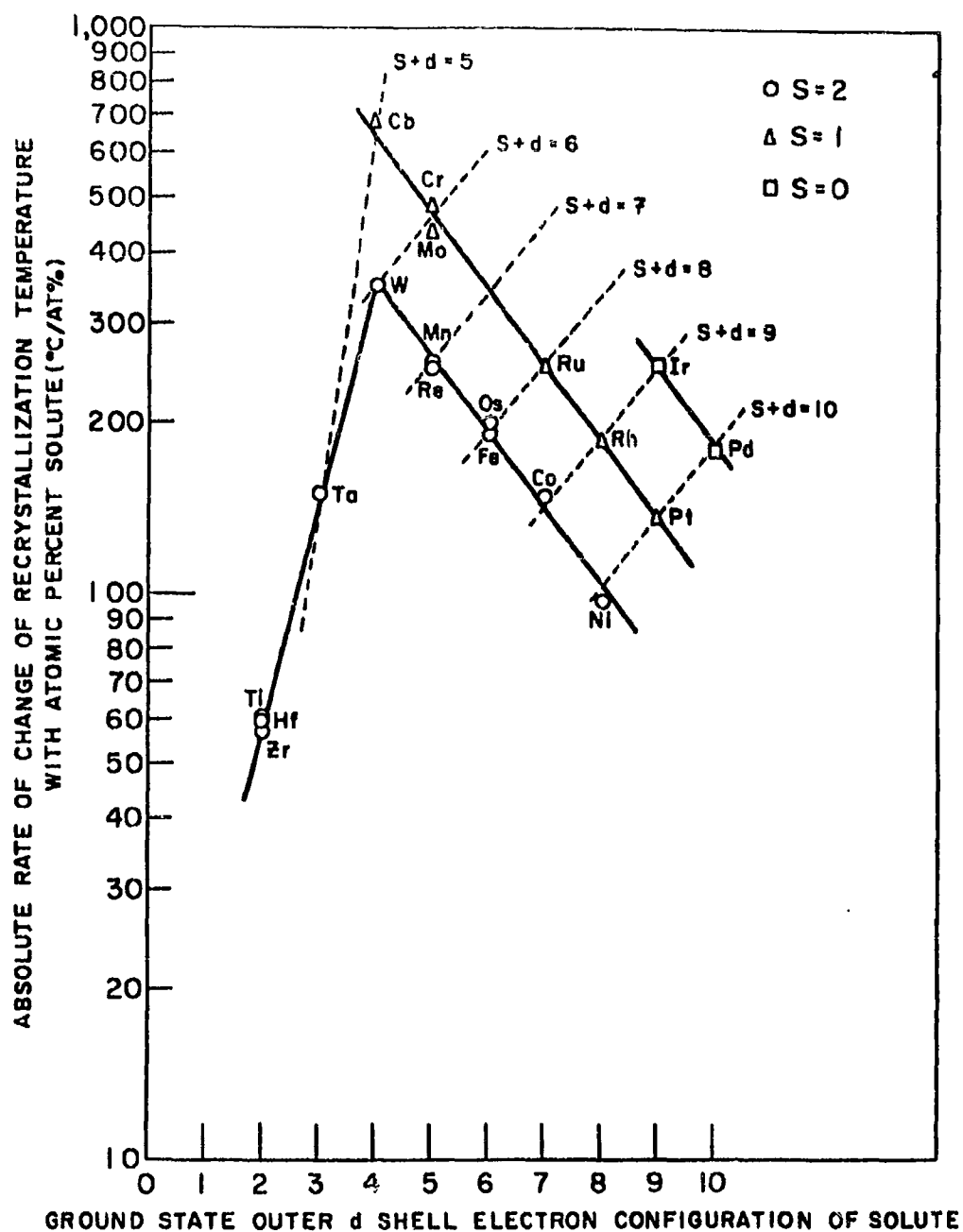
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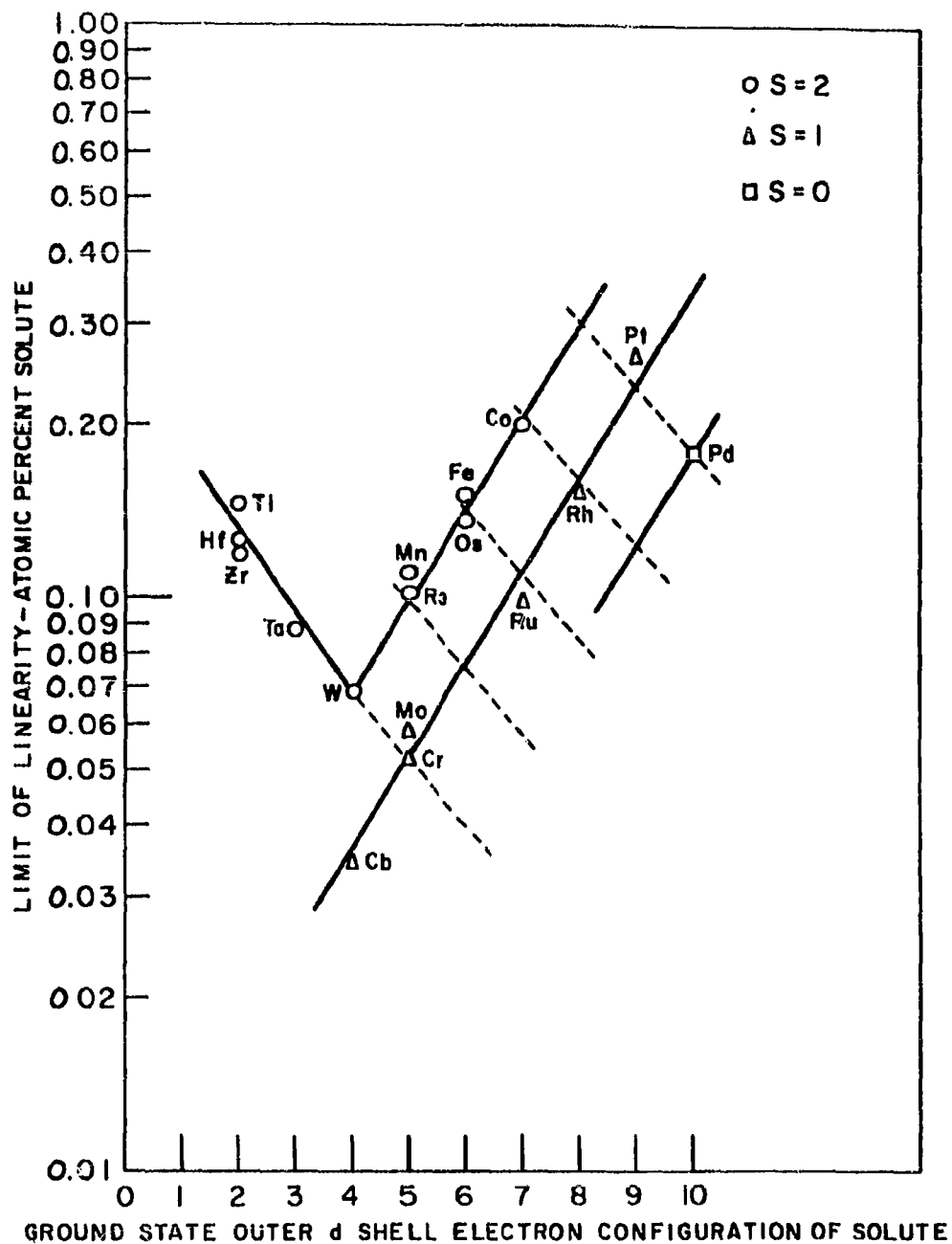
RECRYSTALLIZATION TEMPERATURE VERSUS ATOMIC PERCENT SOLUTE FOR ELEMENTS IN THE SECOND TRANSITION SERIES.



RECRYSTALLIZATION TEMPERATURE VERSUS ATOMIC PERCENT SOLUTE FOR ELEMENTS IN THE THIRD TRANSITION SERIES.



INITIAL RATE OF CHANGE OF RECRYSTALLIZATION TEMPERATURE WITH ATOMIC PERCENT VERSUS NUMBER OF OUTER d SHELL ELECTRONS OF ADDED ELEMENT.



LIMIT OF LINEARITY IN ATOMIC PERCENT SOLUTE
VERSUS NUMBER OF OUTER d SHELL ELECTRONS
OF ADDED ELEMENT.

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