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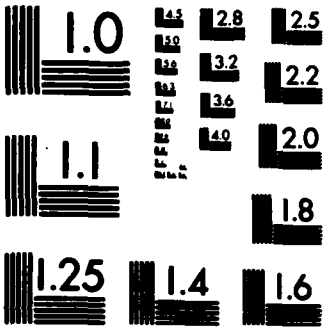

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A MOLECULAR ORBITAL MODEL OF INTERGRANULAR EMBRITTLEMENT

by

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Introduction

Recent attempts to deduce the atomic mechanisms responsible for embrittlement phenomena, specifically intergranular embrittlement in nickel due to segregation of sulfur impurities to grain boundaries, indicates that there is a depletion of intermetallic electron density accompanying the segregation of embrittling agents. This has been interpreted as leading to a weakening of intermetallic bonds with an accompanying reduction in cohesive strength across the grain boundary. While this model is elegantly appealing in its simplicity, it is unable to account for the observed dependence of intergranular embrittlement with the grain boundary concentration of the segregated impurity. This is undoubtedly due to the fact that these studies have ignored the specifics of crack propagation, that is, that brittle fracture occurs when the stress at a crack tip reaches the ideal cohesive strength before it reaches the ideal shear strength. Any model which explains embrittlement as arising from a change in either the the ideal shear strength or the ideal cohesive strength alone, must be considered incomplete.

Exact determinations of ideal cohesive and shear strengths would require very accurate interatomic potentials. In a system modeling a grain boundary containing one or more impurity segregates, the determination of these potentials would be additionally complicated by the lack of information regarding the grain boundary structure and the position of the segregate atoms. It is, therefore, currently beyond the scope of quantum mechanical calculations to give quantitative results concerning the changes in cohesive and shear strengths accompanying impurity segregation. However, simple chemical models supported by quantum mechanical calculations can give information regarding the direction of change in both the shear and cohesive strengths as impurities segregate to grain boundaries. Combining the results of these studies with the one sided studies mentioned earlier provides a complete qualitative understanding of the atomistics of intergranular embrittlement.

Overview

It is widely reported that sulfur, when concentrated in nickel grain boundaries,

produces a brittle system.[1,2,3,4] Studies by C. Loier and J. Boos[5] have revealed that embrittlement is a complicated function of grain boundary sulfur concentration. They have shown that the most dramatic changes in ductile properties occur when the bulk concentrations of sulfur in pure nickel exceed 60 ppm (this corresponds to grain boundary concentrations of about nine atomic percent). At bulk concentrations less than 60 ppm, there is only a very small change in the ultimate tensile strength and the elongation on fracture as compared to pure nickel. When the bulk concentrations reach 100 ppm (14.5 atomic percent intergranular concentration), the ultimate tensile strength has fallen to less than 50 percent of that of pure nickel while the elongation to fracture is only about 40 percent of that observed in pure nickel. In one nickel system, an INCO nickel alloy, there was an increase in the ultimate tensile strength and elongation to fracture as the bulk concentration of sulfur increased from 30 to 60 ppm. W.C Johnson[6] has reported that the embrittlement of "low" sulfur alloys (those having an intergranular concentration of less than 5 atomic percent sulfur) is not caused by the presence of sulfur but rather by the formation of a carbide at the grain boundary. R.M Latanision[7] has produced evidence that suggests that intergranular sulfur is not responsible for embrittlement in nickel alloys containing less than 10 ppm bulk sulfur, while A.W. Thompson[8] has shown that it is the formation of a sulfide that is responsible for intergranular embrittlement in nickel.

Fully quantum mechanical cluster calculations designed to elucidate the atomic mechanisms responsible for the observed intergranular embrittlement have been performed by R.P. Messmer and C.L. Briant.[9,10] They have modeled the segregation of boron, carbon, phosphorus, and sulfur to the grain boundaries of nickel. They have found that sulfur draws charge from neighboring metal atoms onto itself and thereby removes charge from the metal-metal bonds which hold the grain boundary together and weaken them. The tendency to withdraw charge from metal-metal bonds is shown to be greatest for sulfur and to reduce through the series S>P>C>B, with boron actually being a "cohesive inhancer" and not withdrawing charge from the metal-metal bonds. In a later work,[11] it was shown that this tendency to withdraw charge from metal-metal bonds is more pronounced in certain metallic alloys. The impurity preferentially bonds with one of the alloying atoms, thus reducing charge

between this atom and the host metal matrix. W. Losch has arrived at a very similar mechanism for intergranular embrittlement.[12] This model was constructed, however, by drawing an analogy between grain boundaries and free surfaces; results were extracted from quantitative valence bond theory calculations of sulfur chemisorption on nickel model surfaces.

This model can not easily explain the observation that embrittlement seems to suddenly be "turned on" when grain boundary sulfur exceeds a critical concentration. This is probably because these mechanisms fail to consider the role crack tip blunting must play in embrittlement phenomena. J.R. Rice and R. Thompson[13] have demonstrated, in a fundamental paper, that brittle verses ductile behavior is governed at the tip of an atomically sharp crack where the concentrated tensile stress, $\sigma_{\theta\theta}$ ahead of the crack, probe the ideal cohesive strength while the maximum concentrated shear stress, τ_{max} on volume elements inclined by an angle $\theta = \frac{\pi}{8}$ with the two vertical transverse directions, probe the ideal shear strength. This situation is depicted in figure 1. A material will fail in a brittle manner if the ideal cohesive strength is reached along the extension of the crack before the ideal shear strength is reached in the latter mentioned volume element. Alternatively, if the situation is reversed, then the crack tip will be blunted by the nucleation of a dislocation near the crack tip and the material will behave in a ductile manner. Any complete theory of intergranular embrittlement must deal not only with the way the cohesive strength changes as a result of segregation of impurities, but also the effect the segregation has on the shear strength. For only then can it be explained why the segregation of impurities causes a crack located at a grain boundary to propagate in response to loading rather than to blunt.

The models proposed to this point only suggest that metal-metal bonds are weakened in response to impurity segregation. It seems reasonable that this process would also lower the ideal shear stress since, on an atomic scale, the process of shear still requires the breaking of metal-metal bonds. However, while bonds are being broken during shear they are simultaneously being formed. When two planes of atoms are sheared, the distances between some of the atoms of the upper plane

and the lower plane increase; the bonds between these atoms are being broken. However, an equal number of atoms are moving toward each other and bonds are forming or strengthening between these atoms. If the planes being sheared are not homogeneous and the bonds being broken are stronger than the bonds being formed, then these two planes will resist shear more strongly than in the system where the bonds being formed are as strong as the bonds being broken. This is exactly the situation that exists at a grain boundary where impurities have segregated. In a sulfur nickel system, the bulk of the sulfur atoms are located within a few angstroms of the grain boundary. During shear, sulfur-nickel bonds are being broken and not simultaneously being formed. One is tempted to suggest that this would increase the shear strength in the vicinity of the crack tip. However, if these sulfur nickel bonds were sufficiently strong to raise the shear strength, they should also raise the cohesive strength since there are also sulfur-nickel bonds traversing the grain boundary and acting to hold it together. In addition, the presence of strong sulfur-nickel bonds would not explain the observed concentration dependence of sulfur on embrittlement. Yet there is another bond which lies in the plane of the grain boundary and so is broken in the process of dislocation nucleation but, not during brittle fracture, that is the sulfur-sulfur bond.

It may seem unlikely that a bond could form between sulfur atoms which are isolated from each other by an intervening coordination sphere of nickel atoms. However, orbital overlap is maximized when the orbital energies of the overlapping atoms or clusters of atoms are of the same energy. Consequently, there is a tendency for identical atoms to form bonds over great distances when they are placed in a matrix of atoms having different orbital energies.

Calculations and Results

To verify this speculation, SCF-Xα-SW molecular orbital calculations were performed on the Ni_3S_2 cluster shown in figure 2. This cluster was chosen to model the sulfur-sulfur interaction anticipated at a nickel grain boundary. It is assumed that a grain boundary resembles connected Bernal polyhedra. If these polyhedra

each contain a sulfur atom and share a triangular face, then the sulfur atoms would see each other across a triangular plane of nickel atoms as shown in figure 2. The nickel-nickel distances are close packed distances, while the sulfur-nickel distances are those exhibited in sulfur-nickel crystals.

Figure 3 gives the energy eigenvalues for the molecular orbitals resulting from this calculation. This set of energy values is divided into three regions. The lower region corresponds to interactions between sulfur and nickel. The middle region represents interactions between the nickel atoms, and the upper region represents wavefunctions that have a large admixture of sulfur-sulfur interactions. Figure 4 is a contour plot of one of the molecular orbitals from the highest energy region, this plot shows a sulfur-sulfur bond. It has been said that the sulfur-sulfur interaction is a repulsive interaction.[12] This is a meaningless observation, as the sulfur-sulfur distance will be one in which the net force on sulfur atoms is zero, and moving an atom from this equilibrium position will create a force that will act to restore the atom to its original position. Identifying the sulfur-sulfur interaction as repulsive requires the assumption that all interactions are pair wise; this is clearly untrue, for the existence of the sulfur-sulfur interactions over the distances seen in the cluster of figure 2 requires the presence of the nickel atoms.

A Model of Intergranular Embrittlement

It is unusual that such a large region of molecular orbital manifold should be dominated by orbitals with an admixture of sulfur-sulfur interactions. In similar clusters in which boron atoms took the place of the sulfur atoms, the orbitals with boron boron admixture occurred at the Fermi energy.[14] Consistent with this observation is the suggestion that sulfur is able to "see itself" over greater distances than can boron.

These results lead to the following atomistic model of grain boundary embrittlement. As sulfur segregates to grain boundaries, the cohesive strength in the vicinity of the segregate is reduced but so also is the shear strength. At some critical concentration, the segregated sulfur atoms bond with each other forming a network of sulfur-sulfur bonds lying within the grain boundary. At this point, the

shear strength begins to increase while the cohesive strength continues to diminish. These are the conditions necessary for brittle fracture. If the impurity was something other than sulfur, say boron, then not only is there no apparent decrease in the cohesive strength as a result of boron segregation to the grain boundary, but also the critical concentration required for the onset of boron-boron bonds is probably higher than can be realized in a grain boundary.

Finally, if a third atomic species were to be found at a grain boundary which forms three center bonds with the segregate, then the onset of the impurity-impurity bonding network lying in the grain boundary would occur at much lower concentrations. Hydrogen forms such three center bonds and the molecular orbital nature of these bonds has been studied.[15] It is possible that the complexing of hydrogen with grain boundary impurities may explain many of the phenomena described in reference 7. In addition, the preferential bonding shown to exist in reference 11 will produce a network of bonds between the segregated impurity and one of the alloying metal species. This network will lie in the grain boundary and, therefore, raise the shear strength while not effecting the cohesive strength.

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Figure 1

The stress at an idealized crack tip stressed in tension. Volume elements shown are those subject to the maximum shear and tensile stress.

Figure 2

The five atom cluster modeling the sulfur-sulfur interactions at a grain boundary.

Figure 3

The molecular orbital energy values of the five atom cluster of figure 2. Note the extended region of sulfur-sulfur admixture.

Figure 4

A contour plot of the $3a_1$ orbital of the five atom cluster of figure 2. The plot is in a plane containing both sulfur atoms and one nickel atom. Note the very strong sulfur-sulfur bonding interaction.

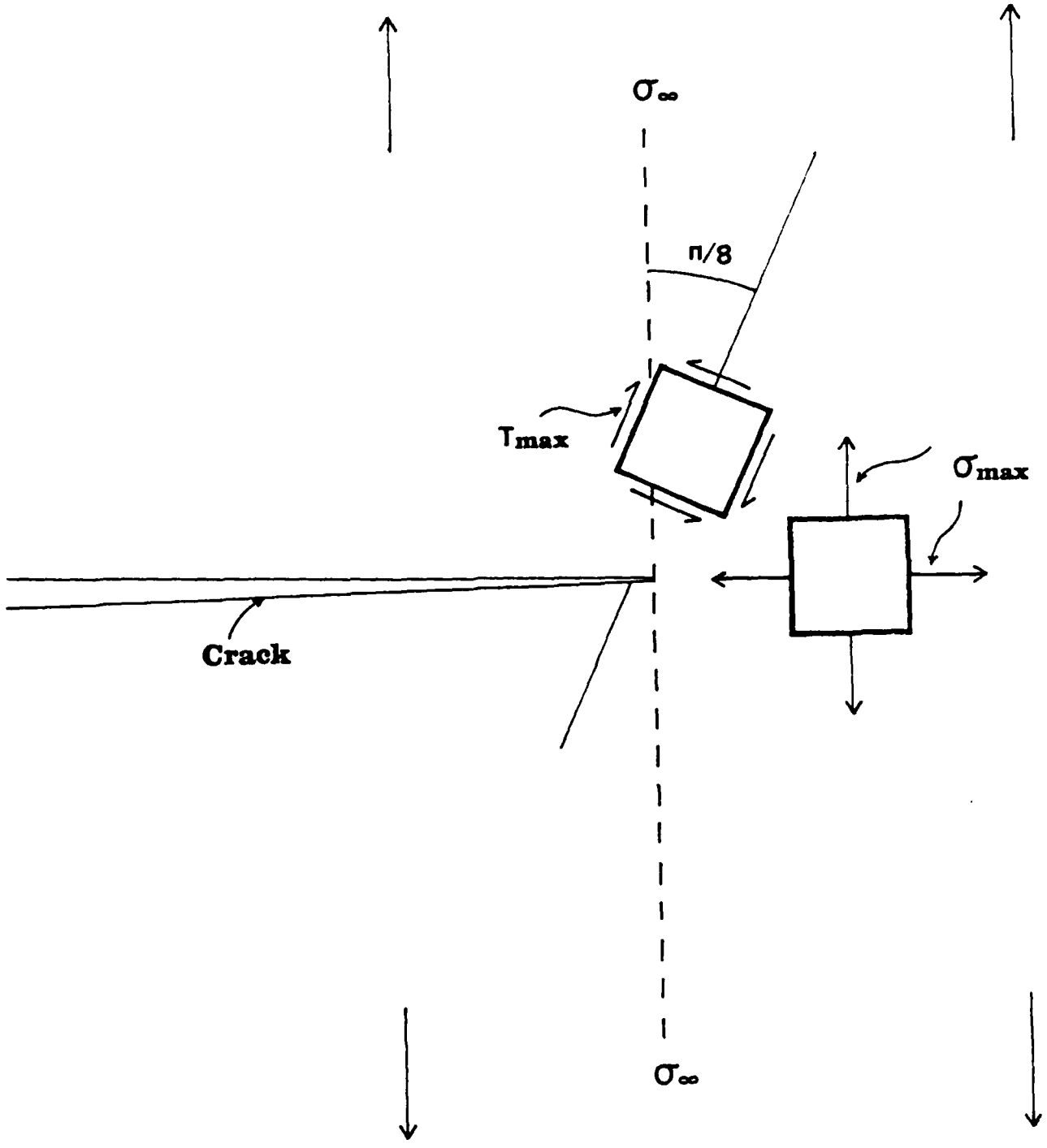

FIGURE 1

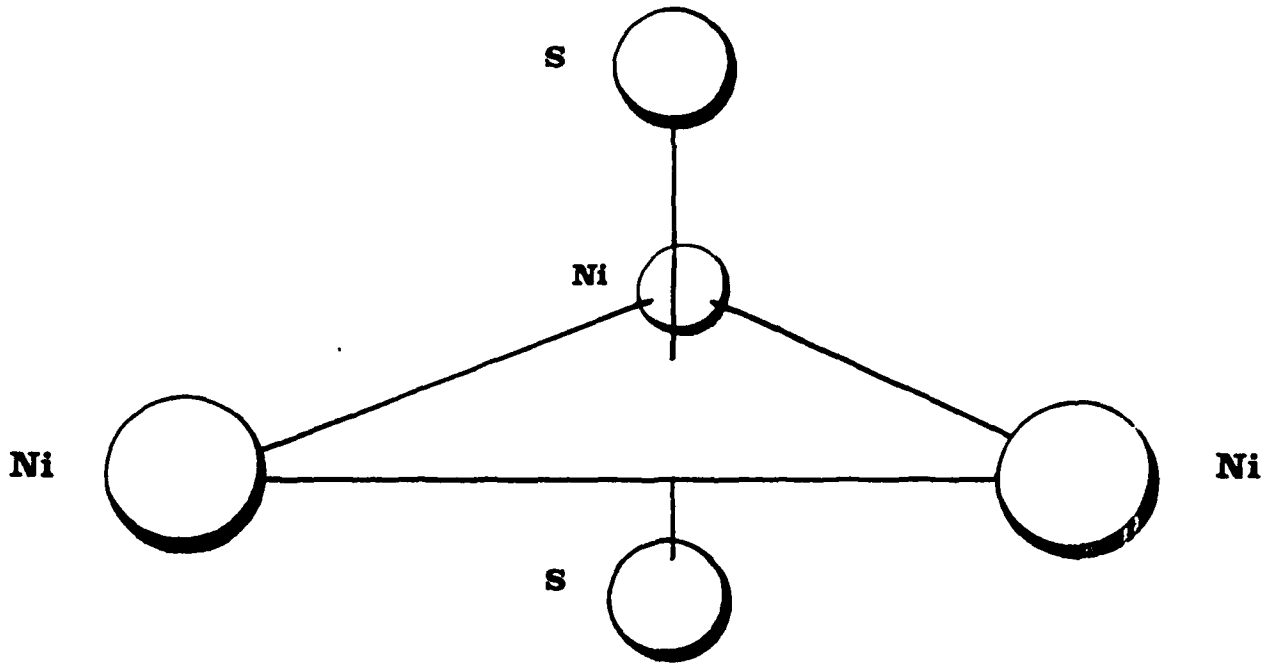

FIGURE 2

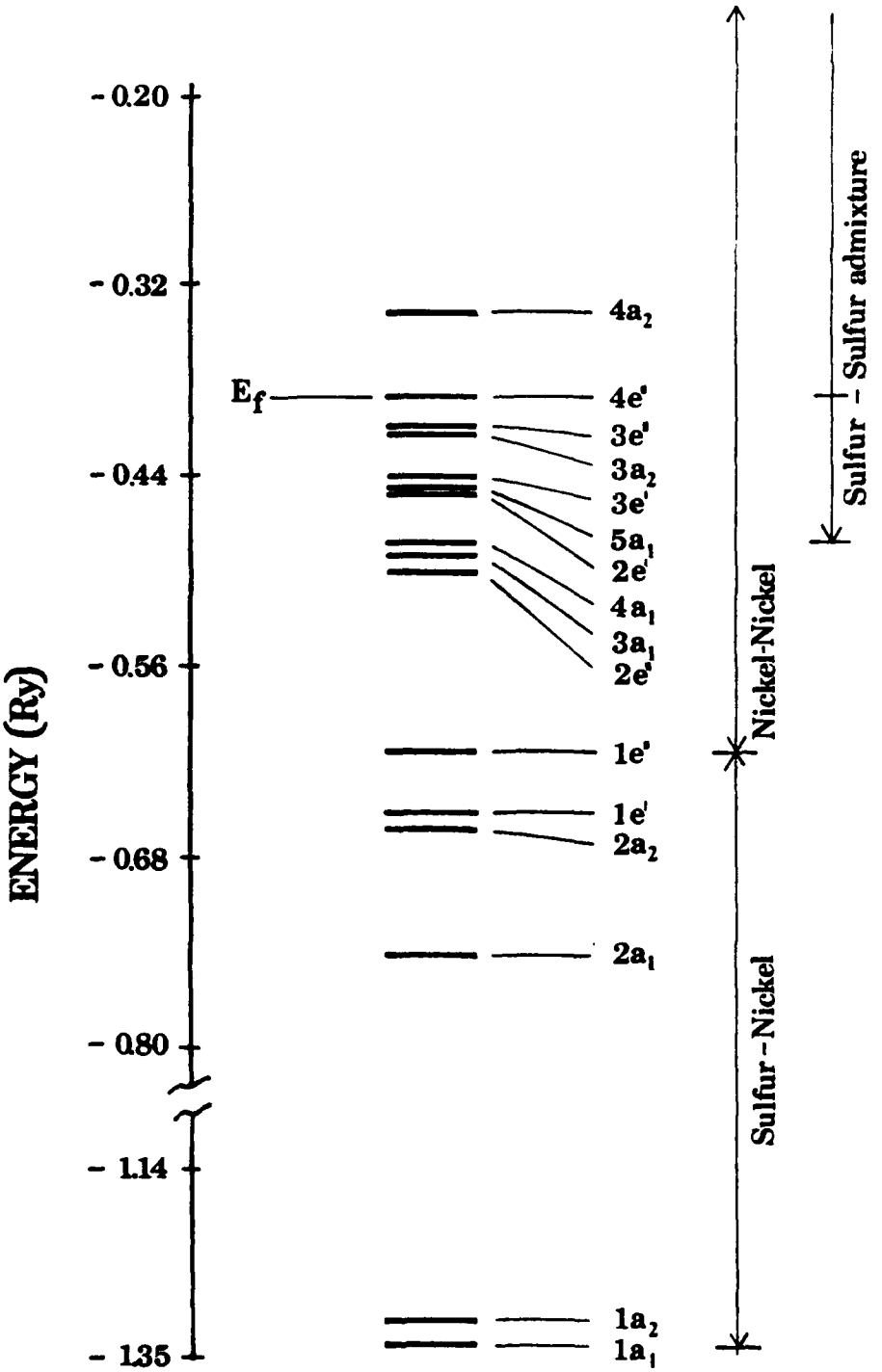
- 0.20
- 0.32
- 0.44
- 0.56
- 0.68
- 0.80
- 1.14
- 1.35
ENERGY (Ry)
E_f
$4a_2$
$4e'$
$3e'$
$3a_2$
$3e'$
$5a_1$
$2e'$
$4a_1$
$3a_1$
$2e'$
$1e'$
$1e'$
$2a_2$
$2a_1$
$1a_2$
$1a_1$
Nickel-Nickel
Sulfur - Nickel
Sulfur - Sulfur admixture

FIGURE 3

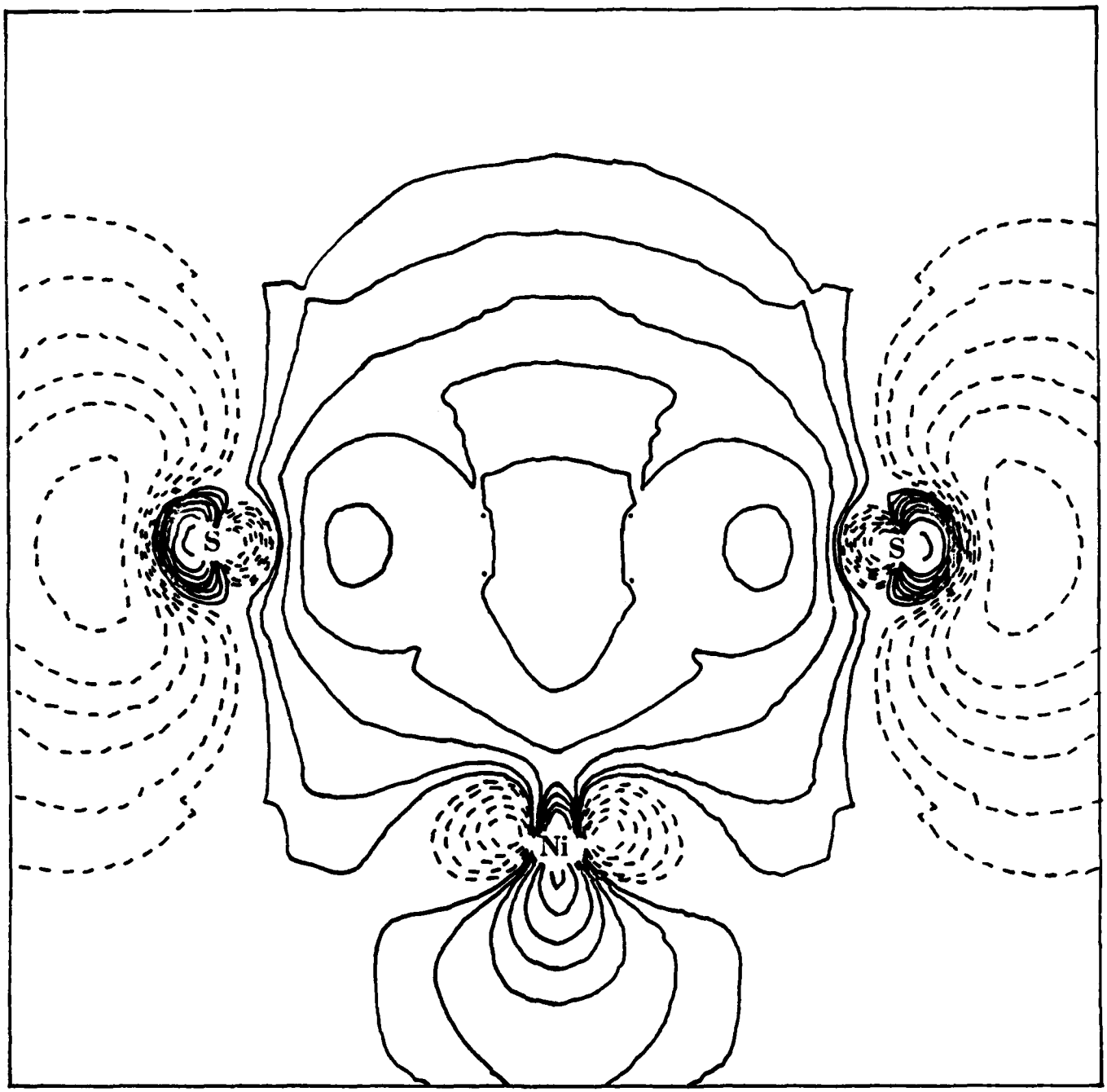

FIGURE 4

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