NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

311.05-11-3110560

October 20, 1969

NBS REPORT

10 061

Progress Report

on

EFFECTS OF COMPOSITIONAL VARIATIONS ON THE ATOMIC ORDERING IN A-15 PHASES

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This investigation was supported in part by Research Grants to the American Dental Association from the National Institute of Dental Research, and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association: the Dental Research Division of the U.S. Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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EFFECTS OF COMPOSITIONAL VARIATIONS ON THE ATOMIC ORDERING IN A15 PHASES

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ABSTRACT

Binary Al5 phases containing only transition elements have been found to possess composition ranges which shift in a regular manner consistent with periodic table positions. This is suggestive of the so-called "electron-compound" behavior previously noted for the sigma phases and other complex structures. It has been shown that deviations from the "ideal" $(A_{a}B)$ composition are accomplished by direct substitution of A-elements and B-elements rather than by vacancy formation. The degree of long-range atomic ordering decreases as one selects elements closer to the manganese column in the periodic table. This effect may be related to the extent of overlapping for d-electron wave-functions particularly along the chains of A-site atoms and is consistent with the band structure model proposed by Labbé and Friedel.

The A-15 structure type may be regarded as belonging to a group of crystal structures which have common crystallographic features and occur in many alloy phases formed by the transition elements. The A-15 phases are remarkable for their stability and for the wide variations in ordering and composition permitted. Although the "ideal" composition is A_3B , stable A-15 phases are found which do not include this composition and in others even the A_3B composition can exhibit considerable disorder.

The cubic unit cell of an ordered A-15-type structure, shown in Figure 1, contains 8 atoms located in two crystallographic positions. Position 6(c) consists of mutually orthogonal atomic chains lying in the cube faces. Position 2(a) consists of atoms located at the cube corners and body-centered position which are crystallographically equivalent for space group Pm3n. The atomic position parameters for both sites are specified by space group symmetry requirements and therefore one may conveniently use x-ray powder diffractometry for order parameter determinations in those cases where the atomic scattering factors for the constituent atoms differ significantly.



• POSITION 2(d) • POSITION 6(c) Figure 1. Cubic unit cell of an ordered A-15 type-structure.

The interatomic distances along the atom chains in position 6(c) are unusually short. This suggests a strong directional bonding but can also be explained by atomic packing considerations. The atomic configuration along the chains is shown in Figure 2. It can be seen that the atoms within the chains are interspersed by planar hexagonal atomic nets which are alternately rotated by 90° about their hexagonal axes. (1) The rotation of these hexagonal networks seems to play an important role in determining the A-15 structure and also in the structure of the sigma phases. In order to accomplish this rotated superposition of hexagonal networks both structures undergo distortions which produce sizable deviations from regularity in the atomic coordination polyhedra at the various crystallographic sites. (1) The atomic coordinations in the A-15 structure are 14 for the atoms in position 6(c) and 12 for the atoms at position 2(a).

2

Phases having the A-15-type crystal structure are generally found to possess a relatively high degree of long-range atomic ordering. All known phases having this structure contain at least one transition element (A-element) from the group (Ti, Zr, V, Nb, Ta, Cr, Mo, W) and these elements show a strong preference for occupying the 6(c) crystallographic lattice sites (A-sites) comprising the orthogonal chains.



Figure 2. Atomic configuration associated with chains of atoms in the A-15 and sigma phase structures. Distances along the A-atom chains are exaggerated for clarity.

The 2(a) crystallographic lattice sites (B-sites) comprising the atoms at the cube corners and the equivalent body-centered position may or may not be occupied by transition elements but are preferred sites for either a non-transition B-element or a transition B-element from the group (Co, Ni, Tc, Ru, Rh, Pd, Re, Os, Ir, Pt, Au).

The relative number of atoms in each of the two crystallographic sites is in the ratio of 3:1 and thus complete ordering into these two sites can occur in a binary alloy only at the composition (A_3B) . This composition is therefore often called the "ideal composition". It has been observed experimentally that many binary A-15 phases occur at or near this "ideal composition". Several reviewers have concluded, on the basis of available data, that ranges of solubility for these phases are more or less invariant around the ideal (A_3B) stoichiometric ratio. (2,3,4,5) With the acquisition of more detailed information, however, it has become apparent that deviations from the ideal stoichiometric composition are not uncommon. Solubility variations of up to 7 percent have been observed on both sides of the ideal composition. Additionally, at least seven binary A-15 phases have solubility ranges which do not even include the ideal stoichiometric ratio (6) Thus, it appears that the forces tending to produce atomic ordering on the two lattice sites are not strong enough to impose a severe restriction on the compositions of these phases. In order to obtain more information on the nature of these forces we have determined the solubility ranges of binary A-15 phases containing first-row transition elements and we have measured the degree of long-range ordering in A-15 phases whose compositions deviate significantly from the ideal stoichiometry. Density measurements were also made in order to deduce whether the existence of lattice vacancies could account for the observed deviations from the ideal composition.

The effect of temperature on the observed long-range order parameters has also been considered but experimental difficulties have restricted the amount of information obtainable at high temperatures. However, we have obtained preliminary data on the A-15 phase $Cr_{72}Os_{28}$ for fast-cooled and for annealed samples examined at room temperature.

In order to facilitate a comparison of the order parameters in the various alloy systems we have in all possible cases annealed our samples at 800°C for one hour to induce maximum ordering. This temperature is well below the decomposition or melting temperature in most cases.

Experimental Procedures

Our alloy samples were arc-melted in an argon-helium atmosphere followed by a high-temperature homogenization anneal in a tantalum-strip resistance furnace in a vacuum of at least 5×10^{-5} torr. Annealing at temperatures below 1100°C was carried out in evacuated fused quartz tubes. The starting materials in all cases had a minimum purity of 99.9 percent and weight losses during melting and annealing did not exceed 1 percent. Composition ranges of the A-15 phases were determined by metallographic examination and by lattice parameter measurements as a function of composition. The heat treatments used are shown in Table 1 together with the range of lattice parameters observed for each binary A-15 phase and the corresponding composition ranges which were determined. Lattice parameters were determined using standard extrapolation methods with a cylindrical powder camera of 114.6 mm diameter.

Measurements of long-range atomic ordering were obtained by using fine powders and a rotating sample holder since preferred orientation at the powder surface was surprisingly difficult to eliminate and is a major factor limiting the accuracy of the order parameter determinations. Fortunately these phases are quite brittle and can be easily crushed to a fine powder without introducing appreciable plastic deformation. This is evidenced by the sharpness of the high-angle lines from the crushed powders. The procedures used in obtaining the long-range order parameters were the same as those used in our previous study. (6)

Density measurements were obtained on single-phase, irregularly-shaped lumps weighing approximately four grams

ELENENTS	A C W Rang e
TRANSITION	Lattice Parameter Range ±0.002Å)*
ING FIRST-ROW	Atomic Radius Ratio (2) $R_{\dot{A}}/_{\dot{W}_{c}}$ (
HASES CONTAIN	Composition (±l atomic %) *
FOR A-15 F	ling ents
RANGES	Annea Treatm
COMPOSITION	Approx. Melt.or Decomp. Temps.

A C N Ranço	6.72 - 6.88	6.48 - 6.78	6.54 - 6.58	6.32 - 6.38	5.95 - 6.60	6.00 - 6.56	6.55 - 6.59	5.75	5.50 - 5.56	5.25 - 5.30
Parameter Range (±0.002Å)*	4.684 - 4.708	4.659 - 4.689	4.681 - 4.699	4.866 - 4.831	4.813 - 4.831	4.785 - 4.798	4.806 - 4.808	5.097	5.034 - 5.025	5.012 - 4.997
Ratio (2) $R_{\rm A}/_{\rm R_{\rm c}}$	0.924	0.945	0.948	0.933	0.970	266.0	0.995	1.014	1.054	1.077
Composition (±l atomic %) *	18 - 22% Pt	16 - 26% Ir	27 - 29% Os	22 - 23% Au	19 - 32% Pt	25 - 39% Ir	52 - 53% Os	25% Au	25 - 26% Pt	25 - 26% Ir
Annealing Treatments	1300°C 24 hrs.	1400°C-24 hrs.	1400°C-24 hrs.	1100°C-5 days	1400°C-24 hrs.	1730°C-10 mins. 1800°C-40 mins.	620°C-1 Yr.	ll00°C-5 days	1100°C-5 days	ll00°C-5 days
Decomp. Temps.	1530°C	1730°C	1540°C	1520°C	1780°C	1930°C	640°C	1395°C	1370°C	1520°C
Binary System	Cr-Pt	Cr-Ir	Cr-Os	V-Au	V-Pt	V-Ir (7)	V-OS	Ti-Au	¶i−Pt	Ti-Ir

* Estimated uncertainty

Table l

using the method of measuring the weight-loss on immersion in distilled water. Small corrections were necessary for the weight of the fine wire used to suspend the sample and for surface tension effects when the wire is immersed in distilled water. These corrections were determined experimentally and amounted to less than 0.1 percent of the observed density values.

Experimental Results

Table 2 lists the order parameters and percentage of site occupancy observed for each of the non-stoichiometric alloys examined in the present study. All samples listed were given a final annealing at 800°C for one hour except V_3 Pd, which was annealed at 800°C for one month. In the V-Pt and V-Ir systems, the order parameters observed were equivalent, within experimental error, to those obtained in our previous studies on the corresponding stoichiometric compositions.⁽⁶⁾ The density values obtained are also shown in Table 2 and agree very well with calculated densities based on the assumption of a direct substitution between A-elements and B-elements. The observed solubility ranges given in Table 1 are illustrated graphically in Figure 3 in order to show the composition shifts characteristic of the so-called "electron compounds". In each binary A-15 phase, except Ti₃Au and possibly V-Os, the lattice parameter variations (see Table 1) indicate a finite range of solubility.



Figure 3. Composition ranges for binary A-15 phase containing first-row transition elements.

The surprising existence of a binary A-15 phase in the system V-Os at approximately the equiatomic composition (7) is herein confirmed. The observed order parameter indicates that this phase is nearly as highly ordered as is possible at this composition. The osmium atoms are essentially filling the 2(a) sites which they would normally occupy as B-elements and INFORMATION CONCERNING THE LONG-RANGE ATOMIC ORDERING IN BINARY A-15 PHASES

Al5 Phase Composition	Order Parameter	Percent Site A	Occupancy Site B	Observed Density	Calculated Assuming Vacancies	Densities* Assuming Substitutio
Vac Ptzo	0.97±0.02	99.4% V 0.6% Pt	21.8% V 78.2% Pt	9.5 ± 0.1	8.91	9.50
V ₇₅ Pt ₂₅	0.98±0.02	99.5% V 0.5% Pt _.	1.5% V 98.5% Pt		1	1
V70 Pt30	0.97±0.02	92.6% V 7.4% Pt	2.1% V 97.9% Pt	11.2 ± 0.1	ġ.27	11.12
V75 IY25	0.94±0.02	98.5% V 1.5% Ir	4.5% V 95.5% Ιr		ł	1
Vee Ir ₃₈	0.91±0.02	80.8% V 19.2% Ir	5.6% V 94.4% Ir	12.6 ± 0.1	8.22	12.59
Vée OS52	0.96±0.04	63.4% V 36.6% Os	1.9% V 98.1% Os	14.8 ± 0.1	7.09	14.74
V, s Pdss	0.69±0.04	92.3% V 7.7% Pd	23.3% V 76.8% Pd	 		ł
* Densities	are calculat	ed using the	e assumptions	s that deviati	ons from the	"ideal"

composition are entirely due to the presence of lattice vacancies. These values are compared with values calculated assuming that the deviations are due to a direct substitution of A and B elements on the two lattice sites.

Table 2

7

the excess osmium atoms must therefore occupy a significant fraction of the atom sites 6(c) normally occupied by A-elements. It appears that in this phase osmium atoms occupy the 6(c) sites in an essentially random manner since no extra lines were observed in the x-ray diffraction pattern of this alloy, nor was there any observable diffuse scattering suggestive of short range ordering.

We have considered the possibility that selective ordering might occur at the B-sites, either on the cube corners or the body-centered positions. An ordered model of this type would produce a new superlattice having a lattice parameter (a,) approximately twice that of the usual A-15-type structure and belonging to space group Fm3 rather than Pm3n. This type of structure has been proposed recently to account for changes in T_c (the superconducting transition temperature) which were produced in the A-15 phase Nb₃ (Al₇₅Ge₂₅) by low-temperature annealing.⁽⁸⁾ It was pointed out that the composition of this phase is exactly suitable for an ordering of Al and Ge atoms in the cube corners and body-centered positions. Such a structure would result in the appearance of new "superlattice lines" in the x-ray patterns as shown in Table 3. Intensity calculations (Table 3) indicate that the superlattice lines (111)(200) and (311) would have intensities of between 0.5 and 1.5 percent of the strongest line in the pattern $\begin{bmatrix} 024\\420 \end{bmatrix}$. Such intensities would lie well within the sensitivity of our diffractometer which has consistently detected lines having intensities corresponding to 0.1% of the main peak intensities for alloy phases of other crystal structures. We have obtained a good powder sample of Nb₃ (Al. 75 Ge. 25) from R. D. Blaugher but we could not detect the superlattice lines predicted by the model of Matthias et al.⁽⁸⁾ We have also carefully searched for and have not been able to detect such lines in our alloy $V_{BO}Pt_{2O}$ for which a similar ordering of Pt and V atoms might be expected on the basis of the alloy composition and for which the superlattice lines should be even more readily detectable due to the ten-fold increase in relative intensity. Small variations in the x and y atomic position parameters from those proposed $(x \approx^{1}/_{\Omega} y \approx^{1}/_{A})$ were attempted but we were unable to reduce the superlattice line intensities to the point where none of them would be detectable.

Thus, it appears that the scheme of ordering proposed in reference 8 does not occur for these alloys despite the favorable compositions. We suspect that any ordering which occurs as a result of low-temperature annealing can be simply ascribed to a random interchange of atoms on the two sites in the A-15 structure without recourse to the larger unit cell.

In order to gain further understanding of the forces responsible for ordering it is of particular interest to study the equilibrium degree of order as a function of temperature. Preliminary results from our $Cr_{72}Os_{28}$ alloy suggest that the forces responsible for ordering in this A-15 phase are of a very different nature from those usually encountered in the CsCl or

A - 15	hkl structure	hkl (Proposed Ordering)	Calculat Relative Inte Nb ₃ (Al _{.75} Ge _{.25})	ed nsities V ₃ (Pt _{.75} V _{.25})
		111	15	150
		200	8	81
	110	220	161	636
		311	9	94
		222	3	28
	200	400	174	480
		331	4	43
	210	$024 \\ 420$	1000	357
	211	422	368	1000

RELATIVE INTENSITIES FOR PROPOSED ORDERING AT THE B-SITES ^{(8)*}

* Only the first nine lines in the pattern are listed.

Cu₃Au type structures. The Bragg-Williams model completely fails to account for the observed behavior even when allowance is made for possible secondary effects. For example, the Bragg-Williams model and some other proposed models predict a sharp temperature dependence for the equilibrium degree of ordering as the temperature approaches the order-disorder transition temperature. However, a sample of the phase Cr₇₂Os₂₈ appeared to have the same order parameter when rapidly cooled from 1400°C as when annealed for one hour at 800°C or for one month at 600°C. This is particularly surprising in view of the very low order parameter (s=0.66) involved here. Thus, the degree of order appears to be relatively temperature-independent in this temperature range. The Bragg-Williams model would predict a strong temperature dependence for an alloy having such a low order parameter. The observed behavior may indicate that the ordering in this phase is not a cooperative phenomenon analogous to ferromagnetism but is more likely related to the electronic band structure as has been previously suggested by Slater (9) and by Nicholas (10) for structures having large numbers of atoms in their unit cells.

Discussion

It can be seen in Figure 3 and Figure 4 that A-15 phases containing Cr and V resemble the Cr and V sigma phases in exhibiting compositions which shift in a regular manner depending on the positions of the constituent elements in the periodic V table. In fact, one can assign a definite range of average group numbers (AGN) to these phases as is often done for the sigma phases and related compounds (Figure 4). There are some definite exceptions to this behavior, however. It does not occur when one of the constituent elements is a non-transition element and it does not seem to apply to A-15 phases containing titanium. In such cases the A-15 phases generally adhere rather closely to the ideal (A₃B) composition with the noteworthy exception of the phase Nb₃Al.



Figure 4. Average group numbers (AGN) for binary sigma phases and A-15 phases.

It is rather surprising that the A-15 phases in the systems V-Ir and V-Pt have such wide solubility ranges while the corresponding phases $Ti_3 Ir$ and $Ti_3 Pt$ adhere quite rigidly to their ideal compositions and possess high order parameters. This contrasting behavior does not appear to be a result of atomic size effects since the atomic radius ratios are not prohibitive (see Table 1). In fact, a rather wide solubility range is also observed for the Nb-Ir A-15 phase despite a difference of 8.2 percent in the atomic radii while Ti_3Au adheres strictly to the ideal composition with only a 1.4 percent difference in the atomic radii. Thus, atomic size effects alone cannot explain compositional variations in the A-15 phases.

On the other hand, it appears that we cannot ignore some of the evidence suggesting atomic packing influences. These influences are revealed in the rotated hexagonal atomic nets and the distortion of the interatomic distances necessary to accommodate this rotation (see reference 1). One also sees unmistakable influences of atomic size effects in the A-atom contractions and the restricted $R_{_{A}}/R_{_{B}}$ ratios within which the A-15 structure occurs. One can see atomic size as a factor in permitting the

occurrence of V-Os and Tc-Mo A-15 compounds at or around the equiatomic composition.

Atomic size relationships, however, cannot explain why some alloy systems which have favorable R_A/R_B ratios do not form the A-15 structure. For example, the V-Ru, V-Ag, Cr-Pd, and Mo-Au systems are noteworthy by the absence of A-15 structures. We could invoke the AGN influences to explain some of these anomalies. However, in many systems where no A-15 compound is observed, both AGN and size factors are favorable. The strongest evidence for the influence of AGN principles (or electron/atom ratio) is found in the observed composition shifts for the compounds of V and Cr. Such influences are notably absent in the corresponding compounds containing titanium or non-transition elements and no obvious relationship between the AGN and the variations in atomic ordering is apparent. Also AGN principles cannot explain the extensive solubility range in the V-Pt A-15 phase, while V₃Pd adheres closely to the A₃B composition.

The tendency for A-15 phases containing non-transition elements or titanium to be highly ordered and adhere closely to the ideal composition is in marked contrast to the behavior of those phases containing osmium. The A-15 phase $V_{4\,8}Os_{5\,2}$, for example, deviates considerably from the ideal composition although it remains as highly ordered as possible at that composition. Conversely, the A-15 phase $Cr_{7\,2}Os_{2\,8}$ deviates only slightly from the ideal composition but possesses a remarkably low order parameter. In both cases, osmium atoms are mixed randomly with vanadium or chromium atoms on the lattice sites. For this mixing to occur, it appears that atomic radius ratios must be favorable. Substitution of niobium atoms for vanadium atoms increases $\frac{R_A}{R_B}$ from 0.995 to 1.085 and leads to the phase Nb₃Os. This phase is rather highly ordered (s=0.90) and occurs at the ideal composition although its solubility range is as yet unknown.

To explain our observations on atomic ordering in the A-15 structures, we propose that the extent of overlapping of the d-electron wave functions is a dominant factor. In a previous study $^{(6)}$ we noted that as elements closer to the manganese column are selected an increasing tendency for disordering occurs (see Figure 5). This effect may be due to a decreasing overlap between A-elements in the orthogonal chains and/or an increasing overlap between A and B elements.

These overlapping d-electron wave functions may be particularly influential in stabilizing the orthogonal A-atom chains since in all known A-15 phases these chains consist primarily of those transition elements generally considered to be capable of strong d-electron overlap. Titanium may be a case for which strong d-electron overlap can occur only with other titanium atoms. This would explain the exclusive occupancy of the Achains (position 6(c)) by titanium atoms and the strict adherence to the ideal composition in A-15 phases containing titanium.

A comparison of our results for the atomic ordering in the V-Pt and V-Pd A-15 phases reveals another rather interesting



Figure 5. Degree of atomic ordering in the A-15-type phases as a function of the position of the constituent elements in the periodic table. (6)

effect. One would normally expect these two phases to exhibit similar behavior in view of the isoelectronic B-elements and similar atomic radius ratios. However, for V-Pt one observes high order parameters and a wide composition range at temperatures up to the solidus while in the V-Pd system the A-15 phase has a rather low order parameter and a narrow composition range. The data on ordering for these two phases suggests an interesting possible explanation for the composition differences.

In the V-Pt system one observes that vanadium and platinum atoms remain exclusively on A and B sites, respectively, until compelled to partially abandon this occupancy by compositional demands. Excess vanadium atoms may then enter B sites until the sites contain about 22 percent V. Alternately, excess platinum atoms may enter the A sites until they contain about 7 percent Pt. In the A-15 phase VaPd, however, atoms in these two sites are mixed simultaneously; each site to the same percentage as in the V-Pt phase, i.e., the B-sites contain about 23 percent V and the A-sites contain 8 percent Pd. This suggests the existence of maximum permissible degrees of mixing for each site. This maximum mixing can apparently be obtained either one site at a time by composition variations or simultaneously (in which case the composition would be automatically fixed). The V-Pt A-15 phase apparently adopts the former method and V₃Pd the latter perhaps as a result of differences in the strength of the d-electron overlap.

One may, therefore, postulate the existence of specific d-electron interactions as a requirement for stabilizing the A-atom chains. The observed composition variations and AGN relationships would then be related to the extent of d-electron overlap along the chains rather than to the overall electron/ atom ratio. In fact, this may also explain the relationship between T_C (the superconducting transition temperature) and the electron/atom ratio as shown by the Matthias regularities. (12,13) We wish to point out, however, that the extent of d-electron overlap along the chains can be influenced by the presence of B-elements in either of the two lattice sites. The actual electron configuration existing along the chains would therefore depend on the location of the B-elements and consequently on the degree of atomic ordering.

The band structure model proposed by Labbé and Friedel⁽¹⁴⁾ provides an attractive explanation for our experimentally observed ordering results. In this model the d-band is split along the A-chains into three sub-bands which are associated with three types of d-orbitals as shown in Figure 6. Our experimental observations that decreasing order parameters are obtained





as one substitutes A-elements closer to the manganese column can be explained by the progressive filling of these d sub-bands. Let us suppose that the titanium phases have a fermi energy which falls within the lowest sub-band corresponding to the $3z^2-r^2$ orbitals. This implies very rigid A-chain occupancy by titanium atoms due to an overlap of these orbitals along the chains. This overlap excludes occupancy of A-sites by B-type atoms, i.e., a high degree of ordering would exist. The vanadium phases can be imagined as lying in the second sub-band. This means that besides the $3z^2-r^2$ orbitals, there are now xZ and yZ type of orbitals which can lead to orbital overlap between vanadium and the B-elements. This could produce an attractive force between them leading to a limited amount of disorder. Finally, the chromium phases could lie in the third sub-band with more complex overlaps and thus a higher potential for disordering.

The fact that the chromium-osmium phase is highly disordered, independent of its thermal treatment, lends credence to the above interpretation. If, in fact, ordering is highly dependent on such a band structure, temperature dependent changes in atomic ordering would be expected to be minimal.

Acknowledgements

We wish to thank R. D. Blaugher of the Westinghouse Aerospace Division for the loan of his sample of $Nb_3 (Al_{.75}Ge_{.25})$ and for helpful discussions. We also wish to thank Mr. R. C. Manuszewski for his work in the dentistry measurements, metallographic studies and some of the x-ray diffraction data. The relative line intensities for the ordering studies were obtained by Miss R. Usatchew and the samples were prepared by Mr. E. Perry. Mr. Howard Swanson of the National Bureau of Standards obtained the x-ray data in our search for weak lines in $Nb_3 (Al_{.75}Ge_{.25})$ and $V_{80}Pt_{20}$ and Dr. Brian Dickens was mainly responsible for programming the intensity calculations. The high-purity vanadium used in this study was given to us by Mr. T. A. Sullivan of the U. S. Bureau of Mines.

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APPENDIX

RELATIONSHIPS BETWEEN THE ORDER PARAMETER (S) AND THE ATOMIC SCATTERING FACTORS (f, AND f_B)

It is rather helpful in understanding the interpretation of the data to examine the relationships between the order parameter (s) and the atomic scattering factors for the the component elements (f_{A} and f_{B} , respectively). The order parameter which we have chosen to use is the usual Bragg-Williams parameter $s = \frac{r_{\infty} - F}{1 - F}$, which has been discussed in a previous publication also in connection with non-stoichiometric compositions.⁽⁶⁾ The contributions of s, f_A, and f_{B} to the structure factor(F) are listed in Table 1 for the . first fourteen lines in the x-ray diffraction pattern for the A15 phase and compared with the same lines in the more familiar CsCl-type and Cu₃Au type of ordered cubic structures. Note that in all of these structures certain lines will disappear when the structure is completely disordered (s=0) and will reappear with the introduction of partial ordering. These lines are often referred to as "superlattice lines" since they are associated with the presence of a "superstructure" produced by the ordering.

15

In the A15 structure, however, fewer lines are of this type. Many lines exist for which the intensities are strongly influenced by the order parameter but which will not disappear when s=0. Some of the lines are quite sensitive to atomic ordering; particularly 110 and 210 as shown in Table 1. Order parameters can be estimated using only these lines if one is careful to obtain good data in this region. In order to guard against possible errors, however, it is well to utilize all lines in the x-ray pattern; particularly line pairs such as 200/211 for which the intensity ratios are independent of atomic ordering and thus serve as a check for preferred orientation effects.

APPENDIX

Table 1

Al5 Structure	Forbidden $2s(f_{B} \cdot f_{A})$ Forbidden $s(f_{B} - f_{A}) + (3f_{A} + f_{B})$ $s(f_{B} - f_{A}) - (3f_{A} + f_{B})$ $s(f_{B} - f_{A}) + (3f_{A} + f_{B})$ $s(f_{B} - f_{A}) + (3f_{A} + f_{B})$ $2s(f_{B} - f_{A}) - (3f_{A} + f_{B})$ $3s(f_{B} - f_{A}) - (3f_{A} + f_{B})$ $s(f_{B} - f_{A}) + (3f_{A} + f_{B})$ $s(f_{B} - f_{A}) + (3f_{A} + f_{B})$ $s(f_{B} - f_{A}) + (3f_{A} + f_{B})$ $2(3f_{A} + f_{B}) + (3f_{A} + f_{B})$
Cu ₃ Au type Structure	$\begin{array}{c} (f_{A} - f_{B}) \\ (f_{A} - f_{B}) \\ (f_{A} + 3f_{B}) \\ (f_{A} +$
CsCl type Structure	$ \begin{array}{c} & (f_{A} \\ f_{A} \\ f_{B} \\ f_{A} \\ f_{B} \\ f_{A} \\ f_{B} \\ f_{$
hkl	100 110 111 200 210 211 220 310, 221 310, 221 311 222 320 400

6(c) normally occupied by A-atoms; f_B denotes the average scattering from sites 2(a) normally occupied by B-atoms. In the other two structures the choice Note: In the Al5 structure, $f_{\rm A}$ denotes the average scattering from sites of A sites and B sites is arbitrary.

17

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT

311.05-11-3110560

December 10, 1969

NBS REPORT

10 127

Progress Report

on

AMINE ACCELERATORS FOR METHACRYLATE RESIN SYSTEMS

I. Synthesis and Color Stability of Composites

by R. L. Bowen and H. Argentar

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This investigation was supported in part by Research Grants DE02494-01 and DE02494-02 to the American Dental Association from the National Institute of Dental Research and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association; the Dental Research Division of the U. S. Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; and the Veterans Administration.

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Amine Accelerators for Methacrylate Resin Systems I Synthesis and Color Stability of Composites

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This investigation was supported in part by Research Grants DE02494-01 and DE02494-02 to the American Dental Association from the National Institute of Dental Research and is part of the dental research program conducted by the National Bureau of Standards in cooperation with the Council on Dental Research of the American Dental Association; the Dental Research Division of the United States Army Medical Research and Development Command; the Dental Sciences Division of the School of Aerospace Medicine, USAF; the National Institute of Dental Research; and the Veterans Administration.

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AMINE ACCELERATORS FOR METHACRYLATE RESIN SYSTEMS I Synthesis and Color Stability of Composites

Abstract

For an investigation of factors that may influence the discoloration and toxicity of polymerization accelerators, tertiary aromatic amines were synthesized with various nitrogen and ring substituents. They were compared with commercial homologs. Composite specimens were prepared based on dimethacrylate monomer formulations with equimolar amounts of these amines being the sole variable. Color stability was influenced more by the nature of the ring substituent than by the kind of the nitrogen substituent. The amine having a <u>p-t</u>-butyl group yielded the most color-stable specimens.

Previous reports have shown that a relationship exists between the structure of an aromatic tertiary amine and the color stability of the methacrylate polymer containing the amine.^{1,2} The color stability decreases in the order:



The hardened specimens containing DMSX [also referred to as DMDA (N,N-dimethyl-3,5-dimethylaniline) previously²] had the lightest color and were the most color stable.

The purpose of this investigation was to prepare and evaluate similar aromatic amines having unusually high molecular weights so as to minimize their solubilities in tissue fluids and thus their freedom to diffuse into the pulp or other tissues.³ Hopefully, such amines would have lower toxicities and produce less pulpal irritation in comparison with the presently used low-molecular-weight amines such as N,N-dimethyl-p-toluidine. This is part of a more general scheme of investigating the feasibility of formulating adhesive dental materials containing no volatile ingredients, and composed entirely of compounds with molecular weights as high as practicality allows. In the extreme, the molecular weights are limited by viscosity and solubility characteristics.

This report will be limited to a description of the methods of synthesis of certain higher-molecular-weight amine accelerators and to the relative color stabilities of composite specimens prepared with various aromatic amines. A separate publication (Part II) is planned for presenting data on the effectiveness of accelerating polymerization. If opportunity permits, comparative toxicity evaluations will be made on the more promising compounds, for subseguent publication.

- 3 -

The tertiary aromatic amines given in Table 1 either were obtained commercially or were synthesized for this investigation. The N,N-dimethylaniline was fractionally redistilled under vacuum before use.

SYNTHESIS OF N-DODECYL-N-METHYL-<u>p</u>-TOLUIDINE (DPT).____ To 20 ml (18.7 gm, 0.014 mol) of N,N-dimethyl-p-toluidine, in a 200 ml, 3-neck round-bottom flask equipped for reflux, 33.3 ml (34.6 gm, 0.14 mol) of n-dodecyl bromide were added and heated under nitrogen atmosphere for 10.5 hours at about 190°C (ranging between 180 and 235°C). The liquid which resulted was distilled at 2 mm Hg pressure. The fraction boiling between 150-200°C was taken to be impure N-dodecyl-N-methyl-<u>p</u>-toluidine. This yielded 19.1 gm (47% of the theoretical yield).

^{*} Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no instance does such identification imply recommendation or endorsement by the National Bureau of Standards or that the material or equipment identified is necessarily the best available for the purpose.

To characterize and attempt purification the hydrochloride salt was prepared and was recrystallized from cyclohexane and washed with petroleum ether. The melting point was 92°C. The amine was regenerated by neutralizing with sodium hydroxide in aqueous methanol. The methanolic solution was extracted with 200 ml of petroleum ether which subsequently dried by filtering through anhydrous sodium sulfate. The petroleum ether was evaporated off by use of an air stream flowing over the solution at a reduced pressure (about 23 inches of mercury). The refractive index n_D^{23} was 1.4920. Carbon, hydrogen and nitrogen analyses were performed on the regenerated amine; calculated for $C_{20}H_{35}N$: C, 83.0; H, 12.2; N, 4.8; found: C, 86.2; H, 13.5; N, 3.4%. The elemental analyses indicate that the product was not pure which may have resulted from the unspecified grade of n-dodecyl bromide (used as received) and from the impracticality of further repurification.

- 5 -

SYNTHESIS OF N-DODECYL-N-METHYL-<u>sym-m</u>-XYLIDINE (DSX).____ Into a 50 ml round-bottom flask were placed 5 ml (4.63 gm, 0.031 mol) N,N-dimethyl-<u>sym-m</u>-xylidine, 7.5 ml (7.8 gm, 0.031 mol) n-dodecyl bromide, and 2.5 ml methanol. The solution was allowed to remain at room temperature for 22 hours and then was refluxed at 70°C for eight hours.

Upon cooling, a waxy solid precipitated. The material was practically insoluble in petroleum ether, acetone, and amyl acetate; partially soluble in hot acetone and very soluble in ethanol. The compound was recrystallized from acetone, washed with ether and ether allowed to evaporate. It had a melting point of 173-175°C.

From the above properties, the compound appeared to be the quaternary compound, dimethyl-dodecyl-<u>sym-m</u>-xylylammonium bromide. It was decomposed by heating with a silicone oil bath to 150-160°C at 3 mm Hg pressure and distilling off volatile material. The bath temperature was finally raised to 195°C resulting in a vapor temperature of 144°C. The material having a boiling point greater than 144°C at 3 mm weighed 4.3 gm (46.0% yield based on amine), had a refractive index n_D^{25} of 1.4842 and a density of 0.91 gm/cc. Anal.: calcd. for $C_{21}H_{37}N$: C, 83.1; H, 12.3; N, 4.6; found: C, 75.2; H, 12.1; N, 2.6%. This lack of agreement indicates impurity probably for the same reasons as with DPT. The melting point of the hydrochloride was 81-82°C when recrystallized from ligroin. A literature search gave no indication that this amine, its hydrochloride or the quaternary ammonium compound had been synthesized previously.

SYNTHESIS OF N, N-DIMETHYL-<u>p</u>-DODECYL ANILINE (DMD).____ To a l-liter round-bottom flask were added 26.3 gm (0.101 mol) <u>p</u>-dodecylaniline, 29.4 gm (0.278 mol) sodium carbonate, 73.1 gm (0.515 mol) methyl iodide, and 500 ml water. The mixture was refluxed for 9.5 hours. The quaternary compound (melting point: 170-172°C when recrystallized from water) was obtained in a 24% yield (10.6 gm) based on the <u>p</u>-dodecylaniline used. A subsequent synthesis furnished another 18.4 gm.

The combined 29.0 gm (0.067 mol) of the quaternary compound was heated in portions to 180°C in a distillation apparatus, whereupon the compound decomposed yielding a

- 7 -

liquid with a boiling point of 43° C; this liquid was probably methyl iodide (lit. b.p. 42.5°C). Heating was continued in each case at 180°C for ten minutes at which time no further decomposition was observed. The various portions of liquid which remained in the distillation flask were combined and totalled 11.3 gm. The liquid had a refractive index n_D^{24} of 1.5095 and was assumed to be N,N-dimethyl-<u>p</u>dodecylaniline. Anal.: calcd. for C₂₀H₃₅N: C, 83.0; H, 12.2; N, 4.8; found: C, 84.1; H, 12.3; N, 4.9%. The yield was 58% of theoretical, based on the quaternary compound. The amine has been prepared previously by a different method of synthesis,⁵ but its properties were not described.

SYNTHESIS OF N, N-DIMETHYL- $\underline{p}-\underline{t}$ -BUTYLANILINE (DMBA).____ The overall synthesis of DMBA was accomplished in 3 parts: synthesis of the corresponding aniline from $\underline{p}-\underline{t}$ -butylbenzoic acid, exhaustive methylation of the compound with the formation of quaternary salt, and subsequent demethylation to DMBA.

- 8 -

SYNTHESIS OF p-t-BUTYLANILINE.___The p-t-butylaniline was synthesized by the technique of Snyder, et al.⁶ Fifty gm (0.30 mol) hydroxylamine sulfate and 594 gm polyphosphoric acid were added to a 1-liter Erlenmeyer flask. The mixture was heated to 145°C and a clear solution resulted. The solution temperature was lowered to 135-140°C and 100 gm (0.56 mol) p-t-butylbenzoic acid was added slowly. The temperature was raised to 155°C and an exothermic reaction took place. The temperature subsequently increased to 175°C without external heating. The solution was then cooled to room temperature and poured over 338 gm crushed ice. The aqueous phase was filtered, neutralized with aqueous potassium hydroxide solution, and extracted with benzene. When 53 ml (57 gm, 0.56 mol) of acetic anhydride were added to the benzene solution, the acetanilide slowly precipitated. Total yield of the acetanilide derivative was 27.8 gm or 26% yield based on p-t-butylbenzoic acid.

Acetanilide (19.2 gm, 0.10 mol) was hydrolyzed by refluxing with 35 ml of 37% hydrochloric acid (0.42 mol) in 55 ml of water for 18 hours. The crude, damp <u>p-t-</u> butylaniline (15.4 gm) was obtained by neutralizing the

- 9 -

acidic solution with aqueous sodium hydroxide and decanting off the oil that formed. No further purification was attempted since the compound was to be used as an intermediate.

SYNTHESIS OF <u>p-t</u>-BUTYLPHENYLTRIMETHYL AMMONIUM IODIDE.____The crude <u>p-t</u>-butylaniline (15.4 gm, 0.103 mol) was mixed with 39.5 ml (90.3 gm, 0.636 mol) methyl iodide, 26.7 gm (0.318 mol) sodium bicarbonate and 550 ml water. The mixture was refluxed for approximately seven hours. On cooling, precipitation of a solid (m.p. 184-186°C) took place. The yield was 24.7 gm, 75% of theoretical based on the amine. Malherbe⁷ reports a m.p. of 182-184°C for the compound.

DEMETHYLATION OF <u>p-t</u>-BUTYLPHENYLTRIMETHYL AMMONIUM IODIDE.____The demethylation was accomplished by the technique of Hünig and Baron.⁸ The <u>p-t</u>-butylphenyltrimethyl ammonium iodide (24.7 gm, 0.077 mol) was refluxed with 23.5 ml (23.7 gm, 0.39 mol) ethanolamine for 12 minutes. The resulting mixture was added to 75 ml water. Two phases resulted. The aqueous (lower) phase was extracted with three portions of petroleum ether totaling 100 ml. The

- 10 -

petroleum ether phases were combined with the original organic phase and the petroleum ether was evaporated off. The yield was 6.5 gm (48% of theoretical). The oil which remained was fractionated. It had a refractive index n_D^{24} of 1.5283 and a boiling range of 143-146°C at 42 mm Hg; according to a nomograph,⁹ this corresponds to a boiling range of about 243-247°C at 760 mm Hg. Anal.: calcd for $C_{12}H_{19}N$: C, 81.3; H, 10.8; N, 7.9; found: C, 81.1; H, 10.7; N, 7.8%. Malherbe⁷ reported that N,N-dimethylp-t-butylaniline is an oil with a boiling point of 250-253°C at 760 mm Hg.

SPECIMEN PREPARATION.____The methacrylate formulation¹⁰ that was used for assessing polymerization-initiating abilities, colors, and color stabilities of these amines, in given in Table 2.

In each case the liquid formulation was mixed with a powder containing 1% benzoyl peroxide with the remaining 99% being powdered fused silica treated with 3-methacryloxypropyltrimethoxysilane. Samples were prepared by mixing fifteen drops of monomer formulation with as much powder as possible yet producing a mix that appeared homogeneous. Empirically, the powder incorporated averaged 69% of the total weight of the specimen. This plastic mass was transferred to a clean, dry glass plate. Glass spacers, 1 mm thick were placed around, but not touching, the mix. A top glass plate was pressed down to the spacers, forcing the material into a circular disc of about 20 mm in diameter.

After the resin had polymerized at room temperature and had aged for at least 24 hours, the specimen was removed from the glass plates, rinsed with 95% ethanol, dried and the color was ranked with the other specimens. It was then placed under the sunlamp for 24 hours to determine the relative color stability, as described previously.² The colors and color stabilities of specimens prepared from the various formulations were ranked visually according to "double-blind" subjective evaluation.

- 12 -

Results

Mixtures prepared with powder containing 1% benzoyl peroxide and the formulations detailed in Table 2, hardened in 2 to 4 minutes, with the exception of N,N-dimethylaniline (DMA) and N,N-dipropylaniline (DPA) which hardened at about 9 and 14 minutes, respectively. The hardening times were longer with mixtures containing amines with bulky nitrogen substituents than with mixtures containing amines having only N-methyl substituents. Alkyl ring substitution (in the <u>meta</u> and <u>para</u> positions) had a minor effect on hardening time, providing that there was at least one alkyl ring substituents.

Color stability was influenced more by the nature of the ring substituent than by the kind of the nitrogen substituent. The amine having a <u>p-t</u>-butyl group yielded the most color-stable specimens. The relative colors and color stabilities of these composite specimens are given in Table 3. Specimens containing either DMA or DPA showed extreme yellowing when subjected to the sunlamp, whereas the other specimens darkened only slightly or not at all.

Summary and Conclusions

The color stability of amine-accelerated methacrylate composites varied considerably with the nature of the aromatic amine employed. Aromatic amines having a 3,5-dimethylphenyl ring (N,N-dialkyl-<u>sym-m</u>-xylidines) discolored less than those with a 4-methylphenyl ring (N,N-dialkyl-<u>p</u>-toluidines) and much less than those with an unsubstituted phenyl ring (N,N-dialkyanilines). A compound apparently not reported in the literature as an accelerator, namely, N,N-dimethyl-<u>p-t</u>-butylaniline, yielded the most color stable specimens of those thus far investigated.

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TABLE 1

TERTIARY AROMATIC AMINE POLYMERIZATION ACCELERATORS INVESTIGATED

Amine	Abbrevia- tion	Source
N-dodecyl-N-methyl-p-toluidine	DPT	Synthesized
N-dodecyl-N-methyl- <u>sym</u> -m-xylidine	DSX	Synthesized
N,N-dimethyl-p-dodecylaniline	DMD	Synthesized
N,N-dimethyl-p-t-butylaniline	DMBA	Synthesized
N,N-dimethylaniline	DMA	Eastman Chemical Co. Fractionally Redistilled Under Vacuum
N,N-dipropylaniline	DPA	Eastman Chemical Co. Eastman Grade
N,N-dimethyl-p-toluidine	DMPT	Eastman Chemical Co. Eastman Grade
N,N-dimethyl- <u>sym</u> -m-xylidine	DMSX	Eastman Chemical Co. Eastman Grade

- 15 -

TABLE 2

LIQUID DIMETHACRYLATE RESIN FORMULATIONS USED FOR

ASSESSING POLYMERIZATION ACCELERATORS

%	Compound	Source
45.6	Bis(2-methacryloxyethyl)isophthalate	Synthesized ¹⁰
36.8	Bis(2-methacryloxyethyl)phthalate	Synthesized ¹⁰
14.54	Bis(2-methacryloxyethyl)terephthalate	Synthesized ¹⁰
2.18	2-hydroxy-4-(2-hydroxy-3-methacryloxy- -propoxy)benzophenone (Permasorb MA)	National Starch & Chemical Corp.
0.55	N,N-dimethyl- <u>sym-m</u> -xylidine or equimolar weight of one of the other aromatic amines for com- parison	Given in Table l
0.20	Butylated hydroxytoluene (Tenox [®] BHT; food grade)	Eastman Kodak Co.
0.14	Di- <u>tert</u> -butyl sulfide	K & K Laboratories, Inc.

TABLE 3

RELATIVE DISCOLORATION CAUSED BY POLYMERIZATION ACCELERATORS

Relative Color	Color Change on Exposure to Sunlamp						
Composites	No Change	Barely Perceptible	Pronounced				
Lightest	N,N-dimethyl- <u>p-t</u> - butylaniline	N,N-dimethyl- <u>p</u> - dodecylaniline					
Intermadiate	N-dodecyl-N-methyl- sym-m-xylidine	N,N-dimethyl- p-toluidine					
Darkest	N,N-dimethyl- sym-m-xylidine	N-dodecyl-N-methyl- p-toluidine	N,N-dimethyl- -aniline				
			N,N-dipropyl- -aniline				

- 17 -

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